

Understanding Molecular Dynamics with Coherent Vibrational Spectroscopy in the Time-domain



Matz Liebel
St. Hugh's College
University of Oxford

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Statement of Originality

The research described in this thesis was carried out by the author between Mai 2010 and September 2014 and includes nothing which is the outcome of work done in collaboration, except where specifically indicated in the text. The use of the first person plural is strictly a matter of style in keeping with standard scientific convention.

Abstract

This thesis describes the development of several spectroscopic methods based on impulsive vibrational spectroscopy as well as of the technique itself.

The first chapter describes the ultrafast time domain Raman spectrometer including the development of two noncollinear optical parametric amplifiers for sub-10 fs pulse generation with 343 or 515 nm pumping.

In the first spectroscopic study we demonstrate, for the first time, that impulsive vibrational spectroscopy can be used for recording transient Raman spectra of molecules in excited electronic states. We obtain spectra of β -carotene with comparable, or better, quality than established frequency domain based non-linear Raman techniques.

The following two chapters address the questions on the fate of vibrational coherences when generated on a reactive potential energy surface. We photoexcite bacteriorhodopsin and observe anharmonic coupling mediated vibrational coherence transfer to initially silent vibrational modes. Additionally, we are able to correlate the vibrational coherence activation with the efficiency of the isomerisation reaction in bR. Upon generation of vibrational coherence in the second excited electronic state of β -carotene, by excitation from the ground electronic state, we are able to follow the wavepacket motion out of the Franck-Condon region. We observe vibrationally coherent internal conversion, through a conical intersection, into the first excited electronic state and are hence able to demonstrate that electronic surface crossings can occur in a vibrationally coherent fashion. Additionally, we find strong evidence for vibronic coupling mediated back and forth crossing between the two electronic states.

As a combination of this work we develop a IVS based technique that allows for the direct recording of background and baseline free Raman spectra in the time domain. Several proof of principle experiments highlight the capabilities of this technique for time resolved Raman spectroscopy.

In the final chapter we present work on weak-field coherent control. Here, we address the question of whether a photochemical reaction can be controlled by the phase term of an electric excitation field, in the one photon excitation limit. We study the systems rhodamine 101, bacteriorhodopsin, rhodopsin and isorhodopsin and, contrary to previous reports, find no evidence for one photon control.

Contents

List of Figures	v
List of Tables	ix
List of Abbreviations	x
1 Introduction	1
2 Theory and background	5
2.1 Nonlinear optics	5
Basic second order interactions	6
Qualitative phase matching	8
Basic third order interactions	11
2.2 (Non)linear spectroscopy	13
Time dependence of wave functions	14
Time evolution of the density matrix	15
Time evolution in the interaction picture	16
The nonlinear polarisation	17
Linear spectroscopy	19
Nonlinear spectroscopy	22
3 Experimental methods	27
3.1 Experimental optics	27
Whitelight probe generation and detection	28
Sub-10 fs pulses from a 515 nm pumped NOPA	32
Sub-10 fs pulses from a 343 nm pumped NOPA	34
>150 fs pulses from a 515 nm pumped NOPA	37
Pulse compression	38
Electric field characterisation by SHG-FROG	40

	Electric field characterisation by SEA-TADPOLE	41
	Amplitude and phase shaping with a spatial light modulator . .	44
3.2	Experimental spectroscopy	46
	Transient absorption spectroscopy	46
	Vibrational coherence	47
	Transient absorption experiments at high temporal resolution .	48
	Chirped whitelight continuum probe	50
	Amplitude dependence of vibrational coherence	52
	Fourier transformation basics	55
	Discrete Fourier transformation basics	56
	Electronic state assignment of vibrational coherences	58
	Frequency estimates of vibrational coherences	61
	Temporal resolution correction	64
4	Observing vibrational coherence on excited electronic states	67
4.1	Introduction	67
4.2	Experimental and Results	69
	Impulsive vibrational spectroscopy of β -carotene	69
	Frequency content of the vibrational coherence	71
	Subtraction in time and frequency domain Raman	72
	Automated subtraction algorithm for impulsive vibrational spec- troscopy	74
	Isolation of pure excited state contributions	76
4.3	Discussion	78
	The excited state Raman spectrum of β -carotene	78
	Time resolved vibrational kinetics of β -carotene	79
4.4	Outlook and Conclusion	81
5	Vibrational coherence of bacteriorhodopsin	83
5.1	Introduction	83
5.2	Experimental results	85
	Bacteriorhodopsin sample	85
	Impulsive vibrational spectroscopy of bacteriorhodopsin	85
	Electronic population control of bacteriorhodopsin	87
	Isolating the pure excited state vibrational coherence of bacte- riorhodopsin	93

The vibrational coherence activity of the excited electronic state of bacteriorhodopsin	94
An unreactive comparison	96
5.3 Discussion	98
5.4 Conclusion and Outlook	102
6 Vibrationally coherent intersystem crossing of β-carotene	103
6.1 Introduction	103
6.2 Experimental results	104
Pre-resonant excitation	104
Resonant excitation	106
Population control	109
6.3 Discussion	112
6.4 Outlook and Conclusion	114
7 Population controlled impulsive vibrational spectroscopy	115
7.1 Introduction	115
7.2 Experimental and results	118
Time resolved pc-IVS of <i>trans</i> -stilbene	119
Time resolved pc-IVS of retinal protonated Schiff base	122
Time resolved pc-IVS of low concentration astaxanthin	125
7.3 Conclusion and Outlook	127
8 On quantum coherent control in the one photon limit	129
8.1 Introduction	129
8.2 Experimental results	132
Pulse shaping considerations	132
Self-referenced weak field coherent control	133
Performance of self-referenced coherent control	134
Weak field self-referenced coherent control	137
Broadband weak field self-referenced coherent control on rho- damine 101	139
Weak field coherent control on bacteriorhodopsin	141
8.3 Discussion	144
8.4 Conclusion and Outlook	146

9 Summary and Outlook	147
9.1 Summary	147
9.2 Outlook	149
Bibliography	153

List of Figures

2.1	Energy level diagrams for $\chi^{(2)}$ nonlinear optical processes	7
2.2	Phase matching of radiating dipoles	8
2.3	Phase matching by angle adjustment between wave vectors . . .	10
2.4	Energy level diagrams for linear spectroscopy	20
2.5	Energy level diagrams for transient absorption spectroscopy . .	23
2.6	Additional energy level diagrams	24
3.1	Whitelight generation and properties	29
3.2	Whitelight detection	29
3.3	Whitelight optimisation and stability	31
3.4	Schematic and performance of a 515 nm pumped sub-10 fs NOPA	33
3.5	Angular distribution of different whitelights	34
3.6	Schematic of the 343 nm pumped sub-10 fs NOPA	35
3.7	Characterisation of the 343 nm pumped sub-10 fs NOPA	37
3.8	Schematic and performance of a 515 nm pumped >150 fs NOPA	38
3.9	Commonly employed pulse compression schemes	38
3.10	Explanation of SHG-FROG and iFROG	41
3.11	SEA-TADPOLE based phase retrieval and reference generation	42
3.12	Spatio-temporal coupling and spatial light modulators	45
3.13	Concept of transient absorption spectroscopy	47
3.14	Concept of vibrational coherence	48
3.15	Data processing, from raw data to Fourier spectra	49
3.16	Whitelight chirp and temporal resolution	51
3.17	Vibrational coherence magnitude	52
3.18	Temporal resolution and vibrational coherence	54
3.19	Preparing vibrational coherences for a discrete Fourier transfor- mation	57
3.20	Illustration of window and zero padding effects	59

3.21	Identifying excited state vibrational coherences	60
3.22	Phase effects on line shapes	62
3.23	Sliding window Fourier transform artefacts	63
3.24	Amplitude correction of Fourier spectra	65
4.1	Potential energy surfaces of β -carotene and pulses employed . . .	69
4.2	Pulses and chopping scheme employed for recording excited electronic state Raman spectra	70
4.3	Electronic kinetics and vibrational coherence of β -carotene in the absence and presence of the actinic pulse	71
4.4	Comparison of the Fourier intensity spectra obtained	72
4.5	Subtraction of solvent contributions from Raman spectra in time or frequency domain	73
4.6	Time domain based subtraction algorithm	74
4.7	Fourier intensity maps and spectra for β -carotene.	77
4.8	S_1 time domain Raman spectrum of β -carotene dissolved in cyclohexane	79
4.9	Following the decay of the S_1 state in β -carotene with vibrational sensitivity	80
5.1	Retinal protonated Schiff base photochemistry	84
5.2	Retinal protonated Schiff base potential energy surface and absorption spectrum	86
5.3	Transient electronic kinetics and vibrational coherence of bacteriorhodopsin (bR)	87
5.4	Vibrational coherence activity and ground state Raman	88
5.5	Electronic population control for the isolation of excited state vibrational coherence	89
5.6	Electronic population control of bacteriorhodopsin	90
5.7	Results of electronic population control of bacteriorhodopsin. . .	91
5.8	Possible signatures of vibrationally coherent photoproduct formation.	92
5.9	Fitting the stimulated emission vibrational coherence	94
5.10	Pure VC activity on the S_1 electronic state of bacteriorhodopsin	96
5.11	Molecular structure of pma-RPSB	97
5.12	Experimental and theoretical Raman spectra for nBu-RPSB and pma-RPSB	97

5.13	Extracting vibrational coherence activity of pma-RPSB	99
5.14	Anharmonic coupling as a mediator for efficient photoisomerisation	100
5.15	Sub-50 fs vibrational coherence rise time	101
6.1	Photophysics of β -carotene	104
6.2	Excited state vibrational coherence in β -carotene with pre-resonant excitation	106
6.3	Absorption spectra of β -carotene and excitation pulse	107
6.4	Transient electronic kinetics and VC of β -carotene	108
6.5	Comparison of the VC activity in the S_1 ESA region of β -carotene	108
6.6	Concept of population control	109
6.7	Electronic population control isolates excited state VC	110
6.8	Fourier intensity map of the excited electronic state VC activity	111
6.9	Spectral content of the VC in the S_2 and S_1 spectral regions . .	111
6.10	Vibronic coupling mechanism	112
7.1	Energy level diagrams for some nonlinear Raman processes . . .	117
7.2	Chopping scheme for time resolved pc-IVS	118
7.3	<i>trans</i> -stilbene structure	119
7.4	Vibrational kinetics of the S_1 electronic state of <i>trans</i> -stilbene .	120
7.5	Comparison of S_1 Raman spectra of <i>trans</i> -stilbene recorded via FSRS and pc-IVS	121
7.6	Experimental parameters for time resolved pc-IVS of nBu-RPSB.	122
7.7	Time resolved pc-IVS of all- <i>trans</i> nBu-RPSB	123
7.8	Vibrational kinetics of the S_1 electronic state of nBu-RPSB . . .	124
7.9	Astaxanthin, structure and photophysics	125
7.10	Time resolved pc-IVS of astaxanthin at low signal levels	126
8.1	Tannor-Rice scheme	129
8.2	Concept of one photon coherent control	132
8.3	Self-referenced coherent control setup	134
8.4	Simulated electric fields for self-referenced coherent control self referenced pulses.	135
8.5	Performance of the self-referenced experiment	136
8.6	Performance of the self-referenced weak field coherent control . .	138
8.7	Broadband weak field coherent control of rhodamine 101	140
8.8	Fitness histograms for the broadband CC on rhodamine 101 . .	141

8.9	Weak field coherent control on retinal protonated Schiff base containing opsin proteins	143
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List of Tables

- 5.1 Fitting results obtained for the dump_{OFF} VC in the 760-840 nm spectral region. Frequencies indicated in bold are assigned to the ground electronic state, frequencies in italic are omitted due to their low frequency nature and hence possible interference with the exponential fit applied to remove the electronic kinetics. . . . 95

List of Abbreviations

APDP Actinic-impulsive pump-dump-probe

APP Actinic-impulsive pump-probe

AXT Astaxanthin

BB-IVS Broadband impulsive vibrational spectroscopy

BBO β -barium borate

bR Bacteriorhodopsin

CA Coherent artefact

CARS Coherent anti-stokes Raman spectroscopy

CC Coherent control

CI Conical intersection

CMOS Complementary metal-oxide-semiconductor

DC Direct current

DFG Difference frequency generation

DFT Discrete Fourier transformation

DMSO Dimethyl sulfoxide

DTT Differential transmission

ECG Effective coherence generated

ESA Excited state absorption

FC Franck-Condon

FFT Fast Fourier transformation

FSRS Femtosecond stimulated Raman spectroscopy

FWHM Full-width-half-maximum

GA Genetic algorithm

GDD Group delay dispersion

GSB Ground state bleach

GVM Group-velocity mismatch

HOOP Hydrogen-out-of-place wagging

IC Internal conversion

iFROG Interferometric second harmonic generation frequency resolved optical gating

IR Infrared

isorho Isorhodopsin

ISRS Impulsive stimulated Raman spectroscopy

IVS Impulsive vibrational spectroscopy

KBW Kaiser-Bessel window

LMA Levenberg-Marquardt algorithm

LPSVD Linear prediction singular value decomposition

NIR Near infrared

NOPA Noncollinear optical parametric amplifier

OD Optical density

OR Optical rectification

pc-IVS Population controlled impulsive vibrational spectroscopy

PDP Impulsive pump-dump-probe

PES	Potential energy surface
PP	Impulsive pump-probe
rho	Rhodopsin
RHO101	Rhodamine101
RINE	Raman initiated by nonlinear emission
RPSB	All- <i>trans</i> retinal protonated Schiff base
RR	Resonance Raman
SE	Stimulated emission
SEA-TADPOLE	Spatial encoded arrangement for temporal analysis by dispersing a pair of light E-fields
SFG	Sum frequency generation
SHG	Second harmonic generation
SHG-FROG	Second harmonic generation frequency resolved optical gating
SLM	Spatial light modulator
SNR	Signal-to-noise ratio
SRCC	Weak field self-referenced coherent control
STSS	Shot-to-shot stability
SWFT	Sliding window Fourier transform
TA	Transient absorption
TL	Transform limit
TOD	Third order delay dispersion
TR³	Time resolved resonance Raman
UV	Ultraviolet
VC	Vibrational coherence

VIS Visible

WF Weak field

WFPO Weak field phase only

YAG Yttrium aluminium garnet

Yb:KGW Potassium gadolinium tungstate doped with ytterbium ions

Chapter 1

Introduction

Molecular transformations are governed by the breaking and formation of chemical bonds. The transition from reactants to products proceeds along a reaction path defined by one, or multiple, vibrational degrees of freedom.^{1,2} Chemical reactions are therefore directly coupled to the vibrational motion with frequencies, for organic molecules, of around $100\text{-}3500\text{ cm}^{-1}$, which translates into oscillatory periods of $10\text{-}300\text{ fs}$. Femtosecond temporal resolution is therefore necessary to follow the molecular movement, and hence any chemical transformation, in real time.^{3,4} The advent of ultrashort laser pulses⁵ has made such observations possible even though only for photoinduced processes. Over the last decades, ultrafast pump-probe spectroscopy has become an indispensable tool for monitoring, and understanding, photochemical processes with applications ranging from gas-phase reactions⁶ to biological processes.⁷

If a short enough pulse is employed in a pump-probe measurement multiple vibrational eigenstates can be superimposed and a nuclear wavepacket is generated. Impulsive simulated Raman spectroscopy (ISRS),^{8,9} as pioneered by the Nelson group, directly measures the coherent vibrational evolution of a molecular ensemble following interaction with such a femtosecond pulse. This feature of ISRS makes it especially appealing for the real time observation of molecular transformations, as already foreseen by the authors in 1985: *"...will be especially interesting when the coherent vibration plays an important role in a material rearrangement such as a phase transition or a chemical reaction..."*. Only two years later the research group of Prof. Ahmed Zewail experimentally realised this prediction by monitoring the photodissociation of ICN¹⁰ and the vibrationally coherent NaI to Na^+I^- reaction,¹¹ an approach they termed "femtosecond transition-state spectroscopy".¹² Fragnito *et al.* extended this concept

beyond diatomics by impulsively generating excited state vibrational wavepackets during the photoexcitation of Nile blue.¹³ Contrary to the comparatively easy to rationalise diatomic dissociation reactions, a theoretical treatment was necessary to explain their observations.¹⁴

The concept of time domain vibrational spectroscopy was eventually expanded towards molecules as large as proteins. Zhu *et al.* succeeded in measuring the coherent nuclear response of myoglobin after photodissociation of an NO ligand initially bound to the metal center.¹⁵ Wang *et al.* detected low frequency oscillations $\sim 60\text{ cm}^{-1}$ in the isomerisation product of rhodopsin after excitation with a 35 fs pump pulse.¹⁶ Even though high frequency vibrational coherences ($>1500\text{ cm}^{-1}$) were readily detected in the form of ground electronic state wavepackets^{17,18} no conclusive observation of similar frequencies on an excited electronic state has been made thus far (that is at the beginning of this work in October 2010).^{19–28}

The topic for this dissertation is motivated by the recent observation of dynamical frequency shift during photoreactions.²⁹ These changes manifested themselves in form of distorted Raman line shapes of the hydrogen out of plane wagging modes in the protein rhodopsin, as detected by femtosecond stimulated Raman spectroscopy (FSRS).^{30,31} ISRS, or impulsive vibrational spectroscopy (IVS),³² directly measures the coherent nuclear response of a molecule after photoexcitation in the time domain. Shifting frequencies should therefore be directly observable in the temporal evolution of the vibrational coherence.

The time domain approach has distinct advantages over a frequency domain measurement as performed in, for example, FSRS. Most experiments, in both time and frequency domain, employ pulses in spectral proximity to electronic resonances. In a time domain picture the temporal evolution of the vibrational coherence is recorded on top of a slowly varying electronic signal. These signals can be removed by, for example, low-pass filtering or fitting to slowly decaying exponential functions. Possible errors in data processing will not effect the information content of the rapidly varying vibrational coherence. The frequency domain description is a Raman spectrum superimposed on a non-trivial background, or in a Fourier picture the real or imaginary part of the Fourier transformation of the temporal evolution of the vibrational coherence on top of the electronic signal. To isolate a Raman spectrum the background has to be subtracted. As the subtraction is performed in a spectrally resolved manner errors can distort the Raman line shape and directly introduce artefacts. The

analysis of the temporal evolution of a vibrational coherence is therefore the far more robust alternative.

Despite its initial success little progress has been made in the development of IVS over the recent years. This can be largely attributed to the difficulties associated with the generation of short (~ 10 fs) pulses which are necessary for detecting vibrational coherence over the full vibrational manifold. Additionally, nuclear wavepacket motion is detected on top of electronic signals which can be orders of magnitudes larger in amplitude. High signal stabilities are therefore necessary if any vibrational coherence is to be recorded in a reproducible fashion. The ratio of electronic to vibrational coherence signal is most likely the reason why the observation of high frequency oscillations in resonant systems is rarely reported even though they are readily obtained in off-resonant experiments. As the coherence is recorded on top of the, often huge, electronic background even small signal fluctuations easily mask the vibrational coherence contribution.

This thesis is arranged as follows:

In Chapter 2 we will outline some theoretical concepts of non-linear optics with emphasis on second-harmonic generation, optical parametric amplification (difference frequency generation) and whitelight generation as these processes form the basis of all spectroscopic experiments presented. Additionally, a description of (non)linear spectroscopy will be given. We will develop, and explain, the energy level diagram formalism which allows for the facile rationalisation of the different signals observed in any nonlinear experiments.

The first half of Chapter 3 describes all optical instrumentation that is necessary to perform highly time resolved transient absorption experiments. Whitelight generation and detection, pulse characterisation, shaping and compression as well as ultrashort pulse generation is described. In particular the design of two noncollinear parametric amplifiers (NOPA), pumped at either 515 or 343 nm, is discussed. The sub-10 fs pulses obtained from these NOPAs, in either the visible or near infrared spectral region, form the major cornerstone of all spectroscopic experiments. The second half of Chapter 3 outlines the main concept of ultrafast IVS. Especially vibrational coherence amplitudes and their spectral dependencies are discussed and a brief introduction to discrete Fourier transformations is given.

In Chapter 4, using the S_1 state of β -carotene as a benchmark system we show, for the first time, that IVS is capable of recording Raman spectra of an electronically excited molecule over the full vibrational manifold of interest.

The coherent vibrational evolution of wavepackets generated by photoexcitation into the Franck-Condon region of bacteriorhodopsin is discussed in Chapter 5. We find evidence for the anharmonic coupling mediated transfer of vibrational coherence activity into initially inactive modes. Additionally, we are able to correlate the coherence activity with the isomerisation efficiency of bacteriorhodopsin.

Chapter 6 explores the fate of vibrational coherence upon electronic surface crossing. We generated wavepackets in the S_2 state of β -carotene and follow their evolution into the S_1 electronic state via internal conversion through a conical intersection. Evidence for strong vibronic coupling as well as coherent recrossing between the S_2 and S_1 electronic states is presented.

The previously reported experiments lead to the development of a technique termed population controlled impulsive vibrational spectroscopy (pc-IVS) which we introduce in Chapter 7. This technique allows for the electronic state specific acquisition of background and baseline free Raman spectra in a purely experimental fashion. We demonstrate the capabilities of pc-IVS by recording spectra of astaxanthin, all-*trans* *n*-butyl retinal protonated Schiff base and *trans*-stilbene as well as comparison of the latter with results obtained by FSRS.

In Chapter 8 weak field quantum coherent control on a variety of systems is discussed. By rigorously eliminating possible sources of control artefacts we find, contrary to previous works, no evidence for one-photon phase only control.

Chapter 9 concludes this thesis and presents an outlook for future work.

Chapter 2

Theory and background

In the following chapter we will give a brief description of nonlinear optics and nonlinear optical spectroscopy. Comprehensive theoretical treatments can be found elsewhere.^{33,34} Additionally, the introduction to nonlinear optical spectroscopy by Peter Hamm³⁵ and the book on ultrafast optics by Andrew M. Weiner³⁶ provide excellent alternatives for the reader interested in experimental implementations.

2.1 Nonlinear optics

The frequency range of any laser is limited by its gain medium. For example, a laser with Yb:KGW (potassium gadolinium tungstate doped with ytterbium ions) as gain medium emits pulses around 1030 nm, as determined by the emission spectrum of the excited ytterbium ions. To extend this tuning range nonlinear optical processes can be exploited, which allow for the generation of additional frequencies. In linear optics, the polarisation $P(t)$ of a system depends on the strength of the interacting optical electrical field $E(t)$:

$$P(t) = \epsilon_0 \chi^{(1)} E(t), \quad (2.1)$$

or for a pulsed electric field:

$$P(t) = \epsilon_0 \int_0^\infty R^{(1)}(\tau) E(t - \tau) d\tau. \quad (2.2)$$

With ϵ_0 being the vacuum permittivity, $\chi^{(1)}$ the linear susceptibility describing the materials response to the electric field and $R^{(1)}(\tau)$ a linear response function describing the contribution to the total polarisation produced at time t . For higher field strengths, which are easily accessible with femtosecond light

sources, the polarisation can be expanded in a power series to account for nonlinear contributions.

$$\begin{aligned}
 P(t) &= \epsilon_0 (\chi^{(1)} E(t) + \chi^{(2)} E(t)^2 + \chi^{(3)} E(t)^3 \dots), \\
 &= \epsilon_0 \sum_n \chi^{(n)} E(t)^n, \\
 &= \sum_n P^{(n)}(t).
 \end{aligned} \tag{2.3}$$

Here ^a, $\chi^{(n)}$ ($n > 1$) are the n th-order nonlinear susceptibilities with the corresponding nonlinear polarisations, $P^{(n)}(t)$. Or for a pulsed electric field:

$$P^{(n)}(t) = \epsilon_0 \int_0^\infty d\tau_n \dots \int_0^\infty d\tau_1 R^{(n)}(\tau_n, \dots, \tau_1) E_n(t - \tau_n) \dots E_1(t - \tau_1). \tag{2.4}$$

With $R^{(n)}$ being the n th-order response function. It is worth noting that the electric fields, $E(t)$, should be described as vector quantities and the corresponding susceptibilities, $\chi^{(n)}$, are therefore tensors of the rank $n+1$. For our theoretical treatment, however, it is sufficient to assume electric fields of the form:

$$E(t) = E_0 e^{(-i\omega t)} + cc. \tag{2.5}$$

Basic second order interactions

Second order interactions are only possible in non-centrosymmetric systems, that is media without inversion symmetry. To understand this requirement we examine the second order nonlinear polarisation in a system with inversion symmetry:

$$P^{(2)}(t) = \epsilon_0 \chi^{(2)} E(t)^2. \tag{2.6}$$

If we invert the sign of the applied electric field the resulting polarisation must flip sign due to symmetry requirements:

$$\begin{aligned}
 -P^{(2)}(t) &= \epsilon_0 \chi^{(2)} (-E(t))^2, \\
 &= \epsilon_0 \chi^{(2)} E(t)^2.
 \end{aligned} \tag{2.7}$$

It follows that

$$-P^{(2)}(t) = P^{(2)}(t), \tag{2.8}$$

^aEquation 2.3 is only valid for loss and dispersionless media

which is only possible for vanishing $\chi^{(2)}$. To discuss the different processes that might occur in non-centrosymmetric media we assume an electric field composed of two different frequencies:

$$E(t) = E_0 e^{(-i\omega_0 t)} + E_1 e^{(-i\omega_1 t)} + cc. \quad (2.9)$$

The combination of Equations 2.6 and 2.9 allows us to compute all electric fields resulting from $\chi^{(2)}$ interactions:

$$\begin{aligned} P^{(2)}(t) = & \epsilon_0 \chi^{(2)} (E_0^2 e^{(-i2\omega_0 t)} + E_1^2 e^{(-i2\omega_1 t)} + cc) \\ & + \epsilon_0 \chi^{(2)} (2E_0^* E_1 e^{(-i(\omega_0 + \omega_1)t)} + 2E_0 E_1^* e^{(-i(\omega_0 - \omega_1)t)} + cc) \\ & + \epsilon_0 \chi^{(2)} (2E_0 E_0^* + 2E_1 E_1^*). \end{aligned} \quad (2.10)$$

The first two terms of Equation 2.10 exhibit twice the original frequencies of either ω_0 or ω_1 , a process called second-harmonic generation (SHG).³⁷ The third contribution describes sum-frequency generation (SFG) and the fourth difference-frequency generation (DFG), electric fields at frequencies of either $\omega_0 + \omega_1$ or $\omega_0 - \omega_1$ are created.³⁸ The terms at zero frequency are responsible for an effect called optical rectification (OR)³⁹ which is important for the generation of terahertz radiation.⁴⁰ OR generates a DC polarisation over the material while the other processes give rise to radiation at new frequencies. Figure 2.1 summarises the first three contributions in the form of energy level diagrams. In SHG two photons are annihilated to form a photon at twice the

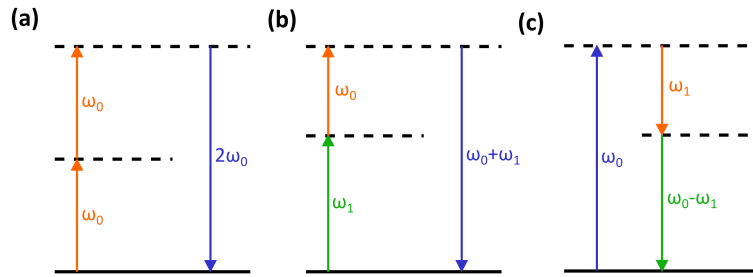


Figure 2.1: **Energy level diagrams for $\chi^{(2)}$ nonlinear optical processes.** (a) Second-harmonic generation. (b) Sum-frequency generation. (c) Difference-frequency generation. The dashed lines represent virtual energy levels with lifetimes dictated by the uncertainty principle through the energy difference to the closest energy level.

frequency (Figure 2.1a). The same is true for SFG but photons of different frequencies contribute to the process (Figure 2.1b). Even though DFG seems,

at first, very similar to SFG its result is fundamentally different. Initially, a photon at ω_0 is destroyed and the system promoted to the excited virtual level. The interaction with the electric field at ω_1 then stimulates the generation of a photon at $\omega_0 - \omega_1$ and, due to energy conservation requirements, at ω_1 (Figure 2.1c). In the process of DFG ω_1 is thus parametrically amplified. Analogous to stimulated and spontaneous emission, from an excited electronic state, two photon emission in the absence of the field at ω_1 can occur, giving rise to the parametric superfluorescence ring⁴¹ which is often exploited in the alignment of noncollinear optical parametric amplifiers (NOPAs).⁴²

From Equation 2.10 it might appear that the processes of SHG, SFG, DFG and OR all happen at the same time. Typically only one of these processes occurs as a result of certain phase matching restrictions, which will be discussed in detail later. Experimentally, one adjusts the electric field polarisations and ensures a favourable $\chi^{(2)}$ by choosing the correct nonlinear crystal, in the appropriate orientation, to enable efficient occurrence of one of the processes.

Qualitative phase matching

In the following we will give a qualitative description of phase matching in nonlinear optical processes. A detailed general description can be found elsewhere,³³ or specifically for the parametric DFG process in NOPA systems in the review article by Cerullo *et al.*⁴² If we assume SHG from a single atom,

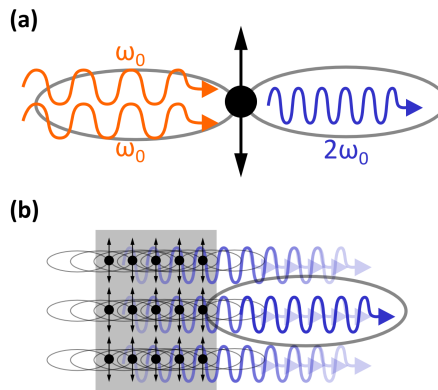


Figure 2.2: **Phase matching of radiating dipoles.** (a) SHG from a single atom. (b) Phase matching governs the emission pattern from a crystal lattice of atoms.

in a non-centrosymmetric environment, the two electric fields at a frequency of ω_0 drive a nonlinear response in form of an oscillating dipole at twice the

frequency, $2\omega_0$. This radiation will be emitted as determined by the dipole emission pattern shown in Figure 2.2a. In a crystal, with atoms at fixed lattice positions, the individual radiation patterns will add up to form a bulk radiation pattern. If the individual patterns are in phase with each other then the overall second-harmonic field scales with the number of radiating atoms and hence the intensity with the square of this number (Figure 2.2b). This condition is called "phase matching condition". Intuitively, we would assume that it should be possible to drastically influence the SHG efficiency by changing the atom to atom distance in a crystal lattice with respect to the electric field. This can indeed be achieved by rotating the crystal shown in Figure 2.2b. Experimentally, this angle dependence has been demonstrated in a quartz crystal.⁴³

The intensity of the second-harmonic signal depends on the wave vector, or momentum, mismatch $\Delta\mathbf{k}$ and the length of the crystal L :

$$I_{SHG} = I_{SHG}^{max} \left(\frac{\sin(\Delta\mathbf{k}L/2)}{\Delta\mathbf{k}L/2} \right)^2, \quad (2.11)$$

with I_{SHG}^{max} being the maximum achievable second-harmonic signal, depending on the incident intensity and the nonlinear susceptibility of the medium, and $\Delta\mathbf{k} > 0$ the wave vector mismatch for SHG defined as:

$$\begin{aligned} \Delta\mathbf{k} &= \mathbf{k}_0 + \mathbf{k}_0 - \mathbf{k}_1, \\ &= \frac{n_0\omega_0}{c}\mathbf{e}_0 + \frac{n_0\omega_0}{c}\mathbf{e}_0 - \frac{n_1\omega_1}{c}\mathbf{e}_1. \end{aligned} \quad (2.12)$$

Here, c is the speed of light and n_i the refractive index at frequency ω_i and $\mathbf{e}_i$ unity vectors. In order to achieve perfect phase matching it is required that

$$\begin{aligned} n_0\omega_0\mathbf{e}_0 + n_0\omega_0\mathbf{e}_0 &= n_1\omega_1\mathbf{e}_1 = n_1(\omega_0 + \omega_0)\mathbf{e}_0, \\ 2n_0\omega_0\mathbf{e}_0 &= 2n_1\omega_0\mathbf{e}_0, \\ n_0 &= n_1, \end{aligned} \quad (2.13)$$

which is commonly not achievable as $n(\omega)$ normally increases monotonically with frequency. Phase matching can still be achieved if birefringent crystals are employed. If one chooses the highest frequency, ω_1 to be polarised in the crystal direction with the lower refractive index then the phase matching condition defined above (Equation 2.13) can be satisfied. Depending on the choice of electric field polarisations and crystal symmetries different phase matching conditions (type I or type II) have been defined.⁴⁴ The often employed β -barium borate crystal can be purchased at specific cut angles with respect to the optical

axis. Since the refractive index is a function of frequency the angle has to be individually adjusted for each application. In the experiment phase matching is fine tuned by tilting the crystal with respect to its optical axis. Phase match-

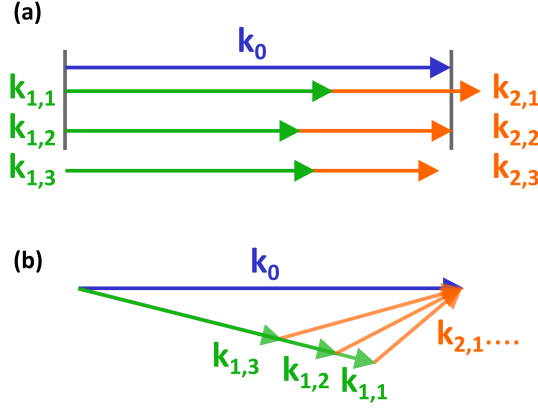


Figure 2.3: **Phase matching by angle adjustment between wave vectors.** (a) In the collinear arrangement of the two initial fields (blue and green) only the DFG process for k_0 , $k_{1,2}$ and $k_{2,2}$ is phase matched. (b) The noncollinear geometry between the initial fields (blue and green) phase matches all DFG processes.

ing conditions can generally be ensured for SHG, SFG and DFG by choosing a correct combination of crystal orientation and electric field polarisations. If large bandwidths are to be amplified phase matching has to be ensured over a broad range of frequencies in the DFG process and the two tuning parameters are no longer sufficient.⁴² To, nevertheless, ensure broadband phase matching it is necessary to introduce an angle between the wave vectors of the two initial fields driving the DFG process. In the collinear arrangement only one of the three possible DFG contributions is phase matched resulting in amplification of a narrow part of the spectrum (Figure 2.3a). If a noncollinear geometry is chosen phase matching can be achieved simultaneously over a broad frequency range (Figure 2.3b). Photons generated at the frequency of the stimulating field, the so-called signal, are emitted into the direction of the respective wave vector where as the electric field at the difference frequency (the idler) is radially dispersed. This phase matching principle of is frequently exploited for the design of NOPAs for femtosecond pulse amplification.

Basic third order interactions

Contrary to $\chi^{(2)}$ interactions third order nonlinear interactions based on the $\chi^{(3)}$ tensor can occur in all media. The third order nonlinear polarisation is described by:

$$P^{(3)}(t) = \epsilon_0 \chi^{(3)} E(t)^3, \quad (2.14)$$

or for a pulsed electric fields as:

$$P^{(3)}(t) = \epsilon_0 \int_0^\infty d\tau_3 \int_0^\infty d\tau_2 \int_0^\infty d\tau_1 R^{(3)}(\tau_3, \tau_2, \tau_1) E(t - \tau_3) E(t - \tau_2) E(t - \tau_1). \quad (2.15)$$

To simplify the expression we assume a monochromatic electric field of the form:

$$E(t) = E_0 e^{(-i\omega_0 t)} + cc. \quad (2.16)$$

By calculating the third order nonlinear polarisation we find contributions at frequencies of either $3\omega_0$ or ω_0 :

$$\begin{aligned} E_0 E_0 E_0 e^{(-it(\omega_0 + \omega_0 + \omega_0))} &= E_0 E_0 E_0 e^{(-i3\omega_0 t)}, \\ E_0 E_0 E_0^* e^{(-it(\omega_0 + \omega_0 - \omega_0))} &= E_0 E_0 E_0^* e^{(-i\omega_0 t)}. \end{aligned} \quad (2.17)$$

We identify the former as being responsible for third-harmonic generation (THG)⁴⁵ while the latter gives rise to an effect at the initial frequency ω_0 that is proportional to the cube of the electric field amplitude E_0 . This second term leads to an intensity dependent refractive index of the form:

$$n = n_0 + n_2 I, \quad (2.18)$$

where n is the total, n_0 the linear and n_2 the second-order index of refraction. As a result of the intensity dependence several phenomena occur, with the easiest to rationalise being self-focusing. If we assume a Gaussian beam and a positive n_2 we find that the refractive index varies with the intensity distribution over the beam profile. A positive lens will be induced as the beam passes through material thus inducing self-focusing. This process can lead to tightly focused filaments within a material and might ultimately cause optical damage. To counterbalance the self-focusing, and hence possible material damage, processes relying on high intensity focused beams, such as DFG in a NOPA, often employ diverging beams within the nonlinear crystals.

Two additional effects occur: self-steepening and self-phase-modulation. We express the phase as a function of wave vector and frequency in a one-dimensional description and insert the intensity dependent refractive index (Equation 2.18):

$$\begin{aligned}\phi(z, t) &= kz - \omega_0 t, \\ &= \frac{2\pi n}{\lambda} z - \omega_0 t, \\ &= \frac{2\pi n_0}{\lambda} z + \frac{2\pi n_2 I}{\lambda} z - \omega_0 t.\end{aligned}\tag{2.19}$$

The frequency can be calculated as the partial derivative of the phase with respect to time:

$$\omega(t) = -\frac{\partial \phi(z, t)}{\partial t} = \omega_0 - \frac{2\pi z}{\lambda} \left(I \frac{\partial n_2}{\partial t} + n_2 \frac{\partial I}{\partial t} \right).\tag{2.20}$$

If we assume a pulse with a Gaussian temporal profile at a carrier frequency of ω_0 then, according to Equation 2.20, new frequencies are generated as a result of the time varying intensity. The processes occurring under this assumption is called self-phase-modulation and leads to the generation of new frequencies. Additionally, self-steepening occurs as a result of the intensity dependent refractive index which leads to a intensity dependent velocity of the pulse. A distorted intensity profile results with, depending on the sign of n_2 , a steep intensity concentration at either the front, or the back of the temporal envelope. The combination of these $\chi^{(3)}$ phenomena can result in the generation of a white light continuum, that is, a spectrally very broad electric field can be generated from an initially narrow spectrum if high intensities are ensured. Even though self-phase-modulation already generates new frequencies⁴⁶ the current hypothesis is that self-focusing in combination with self-steepening generates an optical shock wave that ultimately gives rise to the very broad whitelight.⁴⁷

The combination of second and third-order nonlinear processes allows for the generation of almost arbitrary electric fields from an initially frequency limited source. First, we exploit SHG to double the initial source frequency and, if necessary, additional SHG of the second-harmonic or SFG between second-harmonic and fundamental generates even more frequencies. Electric fields at frequencies far away from the harmonics are accessible by the third-order governed process of whitelight generation with a harmonic of choice. If higher intensities are required then amplification of the whitelight by DFG with a higher frequency harmonic is an option. In short, a narrow bandwidth laser

source can be converted into a frequency tunable spectrometer, the experimental implementation of which will be discussed in Chapter 3.

2.2 (Non)linear spectroscopy

In our description of nonlinear optics we assumed an instantaneous system response. Additionally, we considered atoms and neglected any absorption effects. Previously, we summarised the material response to the incoming electric field by the nonlinear response function $R^{(n)}(t)$, and concentrated on the generation of electric fields with new frequencies. The media applied for nonlinear optics are commonly crystals with certain symmetry properties that allow for selective enhancement of one out of the many possible nonlinear processes. In spectroscopy, however, the main goal is to obtain information about the response function itself, which is now determined by the molecules under study. Knowledge about this function allows for the understanding of the properties, or evolution, of the specific system.

Consider a simple three level system. The electric field might be resonant with an electronic transition and the media is therefore lossy. As a result of the resonance the higher lying electronic state can be populated and the systems response is not necessarily instantaneous. Additionally, once the system has been excited new electronic transitions are possible such as, for example, excitation into the second excited electronic state or a stimulated emission process back onto the ground electronic state. For molecules the situation is even more complex due to the presence of electronic as well as vibrational and rotational energy levels. Spontaneous and stimulated Raman processes are a direct result of the presence of these additional degrees of freedom.

The goal of this section is to explain contributions to the nonlinear polarisation (Equation 2.4) for electric field interactions with a resonant quantum system. By describing the nonlinear response function $R^{(n)}(t)$, as a function of the density matrix, we will be able to rationalise a systems evolution if perturbed by one, or multiple, electric fields. If we knew the precise potential energy surfaces of the system we would be able to quantitatively calculate any experiment. Unfortunately, this is still out of reach for current computational quantum chemistry and we will therefore only use the derived equations to understand signal contributions, signal directions or in general to design experiments that measure a specific property of the system. The energy level diagram

formalism developed throughout this chapter is an intuitive way of describing the evolution of a system under perturbation by an electric light field and it is therefore often not necessary to explicitly solve equations themselves in order to rationalise an experiment.

Time dependence of wave functions

A quantum system is determined by its wave function $\Psi(x, t)$. The time evolution of the system can be described by the time dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = H \Psi(x, t), \quad (2.21)$$

with H being the quantum mechanical Hamiltonian of the system. By assuming $\Psi(x, t) = \psi(x)\chi(t)$, a time-independent Hamiltonian and using Equation 2.21 we can derive a solution for the time dependence of the wave function:

$$\Psi(x, t) = \psi(x)e^{(-\frac{i}{\hbar}\epsilon t)}, \quad (2.22)$$

where ϵ denotes energy. To learn about the temporal evolution of the quantum system we compute its probability density:

$$|\Psi(x, t)|^2 = \left(\psi(x)e^{(-\frac{i}{\hbar}\epsilon t)} \right)^* \psi(x)e^{(-\frac{i}{\hbar}\epsilon t)} = |\psi(x)|^2. \quad (2.23)$$

The result is no longer a function of time and the quantum system is therefore not evolving in time. We note that Equation 2.22 is a particular solution of the time dependent Schrödinger equation and we can, through the superposition principle, replace it by a linear combination of particular solutions:

$$\Psi(x, t) = a_0\psi_0(x)e^{(-\frac{i}{\hbar}\epsilon_0 t)} + a_1\psi_1(x)e^{(-\frac{i}{\hbar}\epsilon_1 t)}. \quad (2.24)$$

The wavefunction is no longer in an eigenstate but in a superposition of states and its temporal evolution is given by:

$$\begin{aligned} |\Psi(x, t)|^2 &= |a_0|^2 |\psi_0(x)|^2 + |a_1|^2 |\psi_1(x)|^2 \\ &+ 2\text{Re} \left(a_0^* a_1 \psi_0^*(x) \psi_1(x) e^{(-i\frac{(\epsilon_1 - \epsilon_0)t}{\hbar})} \right). \end{aligned} \quad (2.25)$$

The first two terms of Equation 2.25 show no time dependence but the third term oscillates with the energy difference between the two states. The temporal evolution of the quantum system is thus entirely contained in the superposition of the two eigenstates which is called a wavepacket or coherence.

Time evolution of the density matrix

We introduce the bra-ket notation where $\langle |$ is called the "bra" and $| \rangle$ the "ket". These vectors contain all the information that can be known about the system, that is, they describe the quantum state of the system. With respect to the wavefunction $\psi(x)$ we define:

$$\psi(x) = \langle x | \psi \rangle = \langle x | \psi \rangle, \quad (2.26)$$

as being the probability amplitude of the system in state $|\Psi\rangle$ to be at position x . From this definition it follows that $\langle \Psi | \Psi \rangle$ must be real and hence:

$$\langle \psi | = |\psi\rangle^*, \quad (2.27)$$

where $|\psi\rangle^*$ is the conjugate complex of $\langle \psi |$.

We are now in a position to introduce the density matrix of a pure quantum state as:

$$\begin{aligned} \rho &= |\psi\rangle \langle \psi|, \\ &= \sum_{n,m} c_n c_m^* |n\rangle \langle m|, \end{aligned} \quad (2.28)$$

here, we expanded ψ in an eigenstate basis of $|n\rangle$. The temporal evolution of the density matrix can be described by the *Liouville-von Neumann* equation:

$$\frac{d}{dt}\rho = -\frac{i}{\hbar} [H, \rho] = -\frac{i}{\hbar} (H\rho - \rho H), \quad (2.29)$$

which is equivalent to

$$\frac{d}{dt} |\psi\rangle = -\frac{i}{\hbar} H |\psi\rangle, \quad (2.30)$$

when considering pure states. In experiments beyond single molecule spectroscopy, however, we generally examine ensembles of molecules. The density matrix allows us to describe statistical averages of different pure states instead of having to treat the joint wave function of all systems and is thus advantageous as experiments are commonly performed on ensembles of systems. We are now in the position to explicitly calculate the temporal evolution of the density matrix, analogous to the temporal evolution of the wave function discussed in the previous section. Again, we choose the eigenstate basis of H as,

$$H = \begin{pmatrix} \epsilon_0 & 0 \\ 0 & \epsilon_1 \end{pmatrix}, \quad (2.31)$$

and the density matrix as,

$$\rho = \begin{pmatrix} \rho_{00} & \rho_{01} \\ \rho_{10} & \rho_{11} \end{pmatrix}, \quad (2.32)$$

to compute the commutator and hence the temporal evolution:

$$\frac{d}{dt}\rho = -\frac{i}{\hbar} [H, \rho] = -\frac{i}{\hbar} \begin{pmatrix} 0 & (\epsilon_0 - \epsilon_1)\rho_{01} \\ (\epsilon_1 - \epsilon_0)\rho_{10} & 0 \end{pmatrix}. \quad (2.33)$$

The diagonal elements, describing eigenstates, show no temporal evolution and the off-diagonal elements evolve in time. The explicit temporal evolution of, for example, ρ_{10} is determined by integration:

$$\rho_{10}(t) = \rho_{10}(0)e^{(-i\frac{(\epsilon_1 - \epsilon_0)t}{\hbar})}, \quad (2.34)$$

and describes an oscillation at the difference frequency, or energy difference, of the coherently superimposed eigenstates, as previously found for the evolution of the wave function.

Time evolution in the interaction picture

During a spectroscopic experiment an electric field weakly perturbs the wave function. The Hamiltonian is now time-dependent and can be written as:

$$H(t) = H_0 + H^I(t), \quad (2.35)$$

where $H^I(t)$ is a small perturbation of the system. Assume there is a unitary operator $U(t, t_0)$ that propagates the state $|\psi(t_0)\rangle$ at time t_0 to the state $|\psi(t)\rangle$ at an arbitrary time, t , later:

$$|\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle, \quad (2.36)$$

then we can express the temporal evolution of the Hamiltonian H_0 as:

$$U_0(t, t_0) = e^{(-\frac{i}{\hbar}H_0(t-t_0))}. \quad (2.37)$$

To describe the temporal evolution of a time-dependent Hamiltonian we define the wave function in the interaction picture in the perturbative limit:

$$|\psi(t)\rangle = U_0(t, t_0) |\psi_I(t)\rangle. \quad (2.38)$$

Now, both the time evolution operator as well as the initial wave function are a function of time. By using the Schrödinger equation $\frac{d}{dt} |\psi(t)\rangle = -\frac{i}{\hbar} H |\psi(t)\rangle$

Equations 2.38, 2.37 and 2.35 we derive an expression for the wave functions evolution as a result of the weak perturbation as:

$$\frac{d}{dt} |\psi_I(t)\rangle = -\frac{i}{\hbar} H_I^I(t) |\psi_I(t)\rangle, \quad (2.39)$$

with $H_I^I(t) = U_0^\dagger(t, t_0) H^I(t) U_0(t, t_0)$ being the weak perturbation operator in the interaction picture. We can iteratively solve Equation 2.39 as:

$$|\psi_I(t)\rangle = |\psi_I(t_0)\rangle + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \dots \int_{t_0}^{\tau_2} d\tau_1 \quad (2.40)$$

$$H_I^I(\tau_n) H_I^I(\tau_{n-1}) \dots H_I^I(\tau_1) |\psi_I(t_0)\rangle.$$

Before action of the propagation operator, $U_0(t, t_0)$, the original and the interaction picture wave function must be identical, that is $|\psi_I(t_0)\rangle = |\psi(t_0)\rangle$. Using Equation 2.38 we can thus rewrite Equation 2.40 as a function of the original wave function:

$$|\psi(t)\rangle = U_0(t, t_0) |\psi(t_0)\rangle + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \dots \int_{t_0}^{\tau_2} d\tau_1 \quad (2.41)$$

$$U_0(t, t_0) H_I^I(\tau_n) H_I^I(\tau_{n-1}) \dots H_I^I(\tau_1) |\psi(t_0)\rangle.$$

To understand the physical meaning of Equation 2.41 we replace the interaction Hamiltonians and use $U(\tau_n, \tau_{n-1}) = U(\tau_n, t_0) U(t_0, \tau_{n-1}) = U(\tau_n, t_0) U^\dagger(\tau_{n-1}, t_0)$ to obtain:

$$|\psi(t)\rangle = U_0(t, t_0) |\psi(t_0)\rangle + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \dots \int_{t_0}^{\tau_2} d\tau_1 \quad (2.42)$$

$$U_0(t, \tau_n) H^I(\tau_n) U_0(\tau_n, \tau_{n-1}) H^I(\tau_{n-1}) \dots$$

$$U_0(\tau_2, \tau_1) H^I(\tau_1) U_0(\tau_1, t_0) |\psi(t_0)\rangle.$$

What is the physical interpretation of this equation? At t_0 the system is described by $\psi(t_0)$ and propagates freely under the propagation operator $U_0(\tau_1, t_0)$ until τ_1 . Here, the operator $H^I(\tau_1)$ interacts with the system which then continues to evolve freely under the action of $U_0(\tau_2, \tau_1)$.

The nonlinear polarisation

As seen previously the temporal evolution of the density matrix, for pure systems, is identical to that of the wave function (Equations 2.29 and 2.30). The same is true for the wave function in the interaction picture (Equation 2.39) and we can therefore expand the density matrix as shown for the wave function

in the last Section. Additionally, we define the perturbation operator in the dipole approximation as:

$$H^I(t) = \mu E(t), \quad (2.43)$$

with μ being the electric dipole operator. We are now able to derive the expressions for the density matrix for $n > 0$ subsequent perturbations:

$$\begin{aligned} \rho^{(n)}(t) = & \left(-\frac{i}{\hbar}\right)^n \int_0^t d\tau_n \int_0^{\tau_n} d\tau_{n-1} \dots \int_0^{\tau_2} d\tau_1 \\ & U_0(t, t_0) [\mu_I(\tau_n), [\mu_I(\tau_{n-1}), \dots [\mu_I(t_1), \rho(0)] \dots]] U_0^\dagger(t, t_0) G(t, 0), \end{aligned} \quad (2.44)$$

where we introduced:

$$\mu_I(t) = U_0^\dagger(t, t_0) \mu U_0(t, t_0), \quad (2.45)$$

as the dipole operator in the interaction picture. The Green function, $G(t, 0)$ prevents backwards propagation in time and thus allows us to integrate from $t = 0$ rather than from $t = -\infty$. The total density matrix is given as the sum over all possible contributions:

$$\rho(t) = \rho^{(0)} + \sum_{n=1}^{\infty} \rho^{(n)}(t). \quad (2.46)$$

The physical meaning of Equation 2.44 is comparable to Equation 2.42 but the dipole operator is now acting on either the Bra or the Ket side of the wave function and the successive action of operators is replaced by the nested commutators $[\dots [\mu_I(t_1), \rho(0)] \dots]$. Additionally, we are able to describe macroscopic ensembles of systems rather than a single wave function. A comparison of the expression for the density matrix with that for the nonlinear polarisation defined previously (Equation 2.4) suggests that we can express the latter as a function of the density matrix. The expectation value of the n th-order nonlinear macroscopic polarisation $P^{(n)}(t)$ is given by:

$$P^{(n)}(t) = \text{Tr}(\mu \rho^{(n)}(t)) = \langle \mu \rho^{(n)}(t) \rangle. \quad (2.47)$$

To relate the form of the equation for the nonlinear polarisation to the experiment we change the definition of the time axis from an absolute: $t, \tau_n, \tau_{n-1} \dots 0$ to a relative axis that reflects the waiting time between perturbations. For example:

$$\begin{aligned} t_n &= t - \tau_n, \\ t_{n-1} &= t - \tau_n - \tau_{n-1}, \\ &\dots \end{aligned} \quad (2.48)$$

We are now in the position to define the n th-order response function:

$$R^{(n)}(t_n, \dots, t_1) = \left(-\frac{i}{\hbar}\right)^n \langle \mu(t_n + \dots t_1) [\mu(t_{n-1} + \dots t_1), \dots [\mu(0), \rho(-\infty)] \dots] \rangle, \quad (2.49)$$

where we substituted $\mu = \mu_I$ for simplicity. This equation allows us to calculate the evolution of the system under the action of arbitrary electric fields.

Linear spectroscopy

Linear spectroscopy describes the interaction with one electric field and it is therefore necessary to solve the equation for the first order polarisation:

$$\begin{aligned} P^{(1)}(t_1) &= \langle \mu \rho^{(1)}(t) \rangle, \\ &= \int_0^\infty dt_1 E_1(t - t_1) R^{(1)}(t_1). \end{aligned} \quad (2.50)$$

To understand the physical meaning of this expression we will first describe the response function by solving the commutator:

$$\begin{aligned} R^{(1)}(t_1) &= -\frac{i}{\hbar} \langle \mu(t_1) [\mu(0), \rho(-\infty)] \rangle, \\ &= -\frac{i}{\hbar} (\langle \mu(t_1) \mu(0) \rho(-\infty) \rangle - \langle \mu(t_1) \rho(-\infty) \mu(0) \rangle). \end{aligned} \quad (2.51)$$

By exploiting the invariance of the trace under cyclic permutation we can rewrite the result as:

$$R^{(1)}(t_1) = -\frac{i}{\hbar} (\langle \mu(t_1) \mu(0) \rho(-\infty) \rangle - \langle \rho(-\infty) \mu(0) \mu(t_1) \rangle), \quad (2.52)$$

which allows us to express $R^{(1)}(t)$ in its final form:

$$R^{(1)}(t_1) = -\frac{i}{\hbar} (\langle \mu(t_1) \mu(0) \rho(-\infty) \rangle - \langle \mu(t_1) \mu(0) \rho(-\infty) \rangle^*), \quad (2.53)$$

with: $\langle \rho(-\infty) \mu(0) \mu(t_1) \rangle = \langle \rho^\dagger(-\infty) \mu^\dagger(0) \mu^\dagger(t_1) \rangle = \langle \mu(t_1) \mu(0) \rho(-\infty)^\dagger \rangle$, which is possible as all operators are Hermitian. We will use the previously introduced energy level diagrams to develop a physical picture behind the commutator. Figure 2.4a shows the representation for the dipole operator acting on the ket side of the density matrix. Initially, the system evolves freely and at $t = 0$ the dipole operator $\mu(0)$, of the electric field $E_0(0)$, perturbs the system. Off-diagonal matrix elements are generated which evolve under the operator $U_0(t, t_0)$. In our graphical representation the system oscillates at the difference frequency between the states e and g as discussed previously (Equation

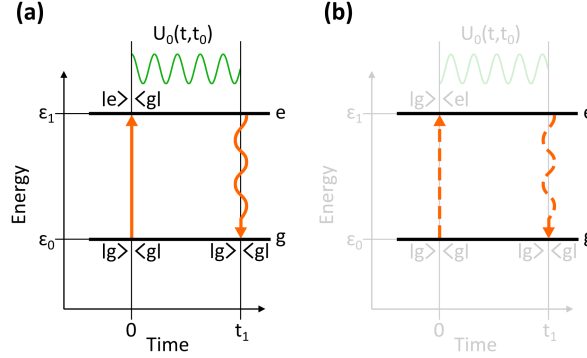


Figure 2.4: **Energy level diagrams for linear spectroscopy.** (a) On the ket side of the density matrix. (b) On the bra side of the density matrix in the commonly used simplified representation. Orange arrows indicate dipole operators, curly arrows the macroscopic polarisation.

2.34). At $t = t_1$ the system returns to its initial state. The same mechanism is possible on the bra side of the density matrix, as can be seen from Equation 2.53. A simplified energy level diagram for this process is shown in Figure 2.4b. Generally, the action of dipole operators on the ket side of the density matrix is indicated by solid and the action on the bra side by dashed arrows. The emission of a macroscopic polarisation is indicated with a curly arrow. Furthermore, most of the extra information shown in Figure 2.4a is omitted and one normally only indicates arrows and energy levels as in Figure 2.4b. Here, we assumed no dephasing of the off-diagonal matrix elements with time, which is a physically inaccurate picture. By using commutators in *Liouville* space it is, however, possible to add specific decoherence models into the propagation operator $U_0(t, t_0)$. The choice of an accurate dephasing model is of great importance when modeling the line shapes observed in 2-dimensional infrared spectroscopy.

For a two level system we can explicitly calculate the expected signals by using Equation 2.53 and the concept introduced when discussing the time evolution of the density matrix.

$$\begin{aligned}
 R^{(1)}(t_1) &= -\frac{i}{\hbar} \langle \mu(t_1) [\mu(0), \rho(-\infty)] \rangle, \\
 &= -\frac{i}{\hbar} \langle \mu(t_1) \begin{pmatrix} 0 & \mu_{10}\rho_{01}(t) \\ \mu_{01}\rho_{10}(t) & 0 \end{pmatrix} \rangle,
 \end{aligned} \tag{2.54}$$

with μ_{xy} being the probability of generating the respective off-diagonal element. The temporal evolution of the off-diagonal elements has been defined previously

(Equation 2.34) as:

$$\begin{aligned}\rho_{xy}(t) &\propto e^{\left(-i\frac{(\epsilon_x - \epsilon_y)t_1}{\hbar}\right)}, \\ &\propto e^{(-i(\omega_{xy}t_1))},\end{aligned}\tag{2.55}$$

action of $\mu(t_1)$ results in:

$$\begin{aligned}R^{(1)}(t_1) &= -\frac{i}{\hbar}\langle\mu(t_1)\begin{pmatrix} 0 & \mu_{10}\rho_{01}(t) \\ \mu_{01}\rho_{10}(t) & 0 \end{pmatrix}\rangle, \\ &= -\frac{i}{\hbar}\langle\begin{pmatrix} 0 & \mu_{10} \\ \mu_{01} & 0 \end{pmatrix}\begin{pmatrix} 0 & \mu_{10}\rho_{01}(t) \\ \mu_{01}\rho_{10}(t) & 0 \end{pmatrix}\rangle, \\ &= -\frac{i}{\hbar}\langle\begin{pmatrix} \mu_{10}^2\rho_{10}(t) & 0 \\ 0 & \mu_{01}^2\rho_{01}(t) \end{pmatrix}\rangle, \\ &= -\frac{i}{\hbar}(\mu_{10}^2\rho_{10}(t) + \mu_{01}^2\rho_{01}(t)), \\ &\propto -\frac{i}{\hbar}\mu_{10}^2(e^{(-i(\omega_{10}t_1))} + e^{(+i(\omega_{10}t_1))}).\end{aligned}\tag{2.56}$$

And we can now evaluate the macroscopic polarisation as:

$$\begin{aligned}P^{(1)}(t_1) &= \int_0^\infty dt_1 E_1(t - t_1) R^{(1)}(t_1), \\ &= -\frac{i}{\hbar}\mu_{10}^2 \int_0^\infty dt_1 E_1(t - t_1) (e^{(-i(\omega_{10}t_1))} + e^{(+i(\omega_{10}t_1))}).\end{aligned}\tag{2.57}$$

We define the electric field to be in resonance with the system:

$$E_1(t) = E_1 e^{-i\omega_{10}t}.\tag{2.58}$$

Insertion into Equation 2.57 yields:

$$\begin{aligned}P^{(1)}(t_1) &= -\frac{i}{\hbar}\mu_{10}^2 \int_0^\infty dt_1 E_1 e^{-i\omega_{10}(t-t_1)} (e^{(-i(\omega_{10}t_1))} + e^{(+i(\omega_{10}t_1))}), \\ &= -\frac{i}{\hbar}\mu_{10}^2 e^{-i\omega_{10}t} \left(\int_0^\infty dt_1 E_1 + \int_0^\infty dt_1 E_1 e^{(+i(2\omega_{10}t_1))} \right).\end{aligned}\tag{2.59}$$

In the rotating wave approximation we can neglect the second term of this expression by assuming that the integral over the rapidly oscillating second term is small compared to the first one. If an infinitely short pulse is employed (impulsive limit) we can replace the electric field by a delta function and solve the integral given in Equation 2.59:

$$\begin{aligned}P^{(1)}(t_1) &= -\frac{i}{\hbar}\mu_{10}^2 e^{-i\omega_{10}(t)} \left(\int_0^\infty dt_1 E_1 \delta(t - t_1) \right), \\ &= -\frac{i}{\hbar} E_1 \mu_{10}^2 e^{-i\omega_{10}(t)}.\end{aligned}\tag{2.60}$$

Since detectors normally measure powers rather than electric fields the signal detected by a spectrometer will be the Fourier transformation of the square of the electric field caused by the polarisation which is a Lorentzian function centered at ω_{10} .

Nonlinear spectroscopy

If more than one electric field interacts with the system the polarisation response becomes nonlinear. In pump-probe, or transient absorption, spectroscopy a pump pulse excites a molecular system of interest by means of two electric field interactions and the generated state is observed by a third interaction with a so-called probe pulse. The nonlinear polarisation is therefore of third order.

To rationalise the possible signal contributions we compute the response function, as previously for linear spectroscopy:

$$\begin{aligned}
 R^{(3)}(t_3, t_2, t_1) &= - \left(\frac{i}{\hbar} \right)^3 \langle \mu(t_3 + t_2 + t_1) [\mu(t_2 + t_1) [\mu(t_1) [\mu(0), \rho(-\infty)]]] \rangle, \\
 &= (\\
 &\quad - \langle \mu(t_3 + t_2 + t_1) \mu(t_2 + t_1) \mu(t_1) \mu(0) \rho(-\infty) \rangle \\
 &\quad - \langle \mu(t_3 + t_2 + t_1) \mu(t_2 + t_1) \mu(t_1) \rho(-\infty) \mu(0) \rangle \\
 &\quad - \langle \mu(t_3 + t_2 + t_1) \mu(t_2 + t_1) \mu(0) \rho(-\infty) \mu(t_1) \rangle \\
 &\quad + \langle \mu(t_3 + t_2 + t_1) \mu(t_2 + t_1) \rho(-\infty) \mu(0) \mu(t_1) \rangle \\
 &\quad - \langle \mu(t_3 + t_2 + t_1) \mu(t_1) \mu(0) \rho(-\infty) \mu(t_2 + t_1) \rangle \\
 &\quad + \langle \mu(t_3 + t_2 + t_1) \mu(t_1) \rho(-\infty) \mu(0) \mu(t_2 + t_1) \rangle \\
 &\quad + \langle \mu(t_3 + t_2 + t_1) \mu(0) \rho(-\infty) \mu(t_1) \mu(t_2 + t_1) \rangle \\
 &\quad - \langle \mu(t_3 + t_2 + t_1) \rho(-\infty) \mu(0) \mu(t_1) \mu(t_2 + t_1) \rangle) \left(\frac{i}{\hbar} \right)^3.
 \end{aligned} \tag{2.61}$$

By using the energy ladder diagrams introduced previously and assuming a system with three electronic levels we can rationalise the signals arising from the response function. Additionally, we assume time ordering, that is the electric field interactions are happening in a pre defined temporal order. The first two electric field interactions come from the pump electric field and the following interaction is with the probe. Figure 2.5 shows a graphical representation of the eight terms obtained from Equation 2.61. A total of six contributions

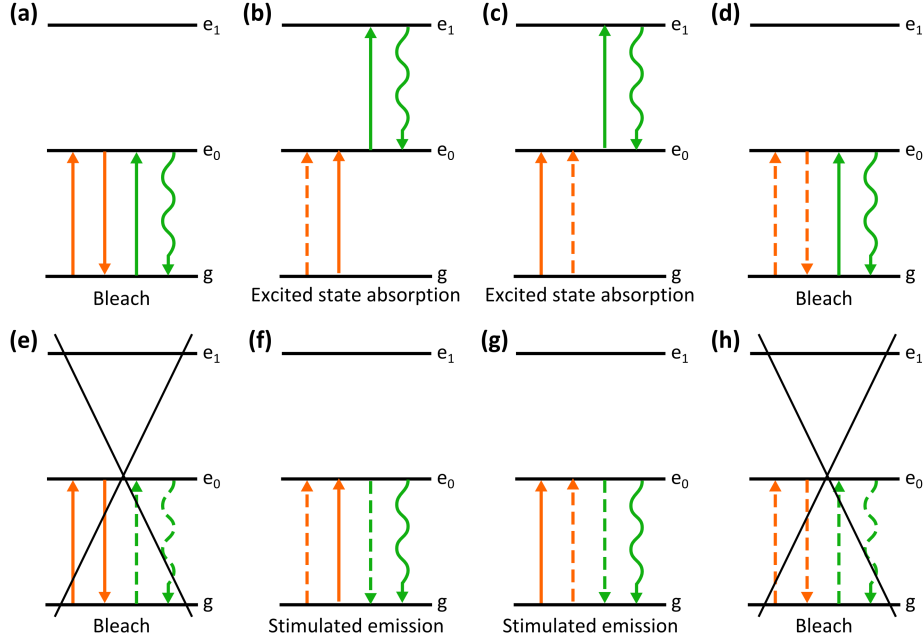


Figure 2.5: Energy level diagrams for transient absorption spectroscopy (a-h). Straight orange arrows indicate pump, green arrows probe interactions. Solid lines are ket, dashed lines bra interactions. The curly arrow is the signal polarisation. It is emitted in the direction of the wave vector of the probe. The crossed out diagrams are not observed under the rotating wave approximation.

survive the rotating wave approximation made earlier. These are: two bleach, two stimulated emission and two excited state absorption contributions. The only difference between the two identical contributions is the order of pump interactions with bra and ket. In the case of nonlinear optics a desired processes can be selected by choosing a specific interaction medium. In a spectroscopic measurement the number of interactions contributing to the nonlinear macroscopic polarisation can be reduced by adjusting the electric field frequencies. It is thus possible to specifically address electronic resonances of interest. In the rotating frame approximation all other, non-resonant contributions, will be eliminated from the macroscopic polarisation.

So far, we have neglected the spatial direction of the electric field:

$$E_0 e^{(-i\omega t + k\mathbf{z})}, \quad (2.62)$$

where k is the wave vector and $\mathbf{z}$ a unity vector. The macroscopic polarisation will be emitted in the direction of the sum of all field interactions. In all six

surviving signal contributions above the direction is:

$$\begin{aligned} \mathbf{k}_{\text{signal}} &= \pm \mathbf{k}_{\text{pump}} \mp \mathbf{k}_{\text{pump}} + \mathbf{k}_{\text{probe}}, \\ \mathbf{k}_{\text{signal}} &= \mathbf{k}_{\text{probe}}, \end{aligned} \quad (2.63)$$

which is in the direction of the probe pulse. Several other interactions often observed in transient absorption spectroscopy remain to be discussed: the coherent artefact, or coherent spike,^{48,49} coherent vibrational oscillations caused by impulsive Raman scattering⁵⁰ and vibrational coherence generated on an electronic state while populating the latter. The first of the described interac-

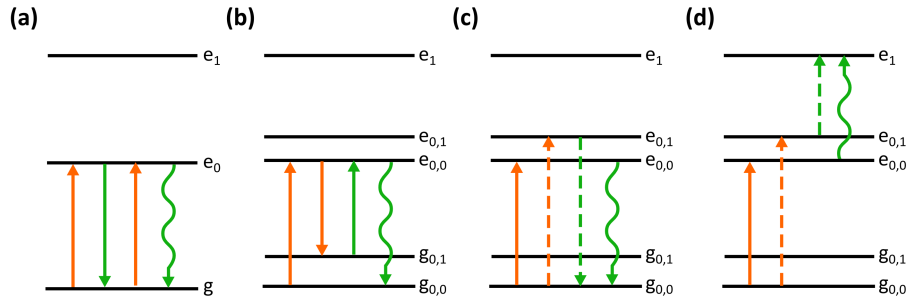


Figure 2.6: **Additional energy level diagrams.** (a) Example of an interaction leading to the coherent artefact. (b) Example of impulsive stimulated Raman. (c) Excited state vibrational coherence generated by photoexcitation from the ground electronic state and observed in the stimulated emission. (d) as (c) but for an excited state absorption signal.

tions occurs if pump and probe pulses temporally overlap, the assumption of strict time ordering therefore loses validity and new signal contributions have to be considered an example of which is shown in Figure 2.6a.

Coherent oscillations can be understood if broad electric fields are considered. Rather than using a system consisting of three electronic states we define a system composed of three electronic states with additional vibrational levels. Interaction with the energetically broad pump pulse superimposes the vibrational levels on the ground electronic state, a vibrational coherence is generated (Figure 2.6b). This coherence is probed by interaction with the probe pulse which leads to a frequency shifted signal field. This process also can occur if the pump pulse is not resonant with the excited electronic state, but at a much lower probability. If the pump pulse is resonant with an electronic transition and energetically broad enough to reach multiple vibrational levels on the excited electronic state a vibrational coherence can be generated during population transfer to the respective electronic state (Figure 2.6c,d). Depending

on the resonance conditions of the probe pulse this vibrational coherence can either be probed in resonance with the ground (Figure 2.6c) or with another excited (Figure 2.6d) electronic state. Comparison of Figures 2.5 and 2.6(b-d) shows that the latter pathways are nothing else than probing bleach, stimulated emission and excited state absorption transitions in the presence of vibrational coherence. The energy of the resulting signal fields is therefore shifted by the energy level spacing of the superimposed vibrational levels.

Chapter 3

Experimental methods

Parts of this chapter have been adapted from the following publications: Liebel, M., Kukura, P., *J. Phys. Chem. Lett.* **2013**, 4, 1358-1364⁵¹ and Liebel, M., Schnedermann, C., Kukura, P., *Opt. Lett.* **2014**, 39, 4112-4115.⁵² The first paper was reprinted with permission from Liebel, M., Kukura, P., *J. Phys. Chem. Lett.* **2013**, 4, 1358-1364. Copyright 2013 American Chemical Society. The second paper was published in Optics Letters and is made available as an electronic reprint with the permission of OSA. The paper can be found at the following URL on the OSA website: <http://dx.doi.org/10.1364/OL.39.004112>. Systematic or multiple reproduction or distribution to multiple locations via electronic or other means is prohibited and is subject to penalties under law. Christoph Schnedermann kindly recorded the pulse spectra of the >150 fs NOPA.

3.1 Experimental optics

The work presented in this and all subsequent chapters was performed using a Lightconversion Pharos-6W laser system as the light source. This Yb:KGW amplifier system outputs 600 μJ pulses centered at 1030 nm with a pulse duration of ~ 200 fs at 10 kHz repetition rate. After splitting off 50 μJ for multiple whitelight (WL) generation stages the 550 μJ of residual fundamental are frequency doubled³⁷ in a type I phase matched $\theta=23.4^\circ$ β -barium borate (BBO) crystal. Following sum-frequency generation³⁸ between the fundamental and the second harmonic in a type II phase matched $\theta=62.8^\circ$ BBO crystal both 515 nm and 343 nm are available for pumping several WL amplification stages.

Whitelight probe generation and detection

Whitelight (WL) generation⁵³ is a convenient mechanism to extend the frequency range of a laser system beyond its harmonics. The initially weak WL is often amplified, ultimately giving access to widely tunable, high energy, pulses. As the WL forms the basis for most of the follow up processes its spectral content, mode quality and stability are of utmost importance. Even though a WL generation stage is easy to implement (Figure 3.1a) the different WL generation parameters such as input power, focal length, lens-bulk material distance, pulse duration and mode quality should be fine adjusted with great care.

Whitelight generation

The WL probe pulse is generated by focusing 1.5-4 μJ of fundamental into a 3 mm sapphire plate by means of a 100 mm focal length achromatic lens. The emerging WL is collimated with a 50 mm focal length curved mirror while keeping the reflection angle to a minimum. After removing residual fundamental with a harmonic separator the WL is used as a broadband probe pulse.⁴⁸ The key factor for obtaining a spectrally uniform and long-term stable WL is a high quality fundamental mode focused at an appropriate numerical aperture.⁵⁴ For a given laser system it is thus advisable to systematically screen several focal length lenses and beam diameters in order to allow for the best possible WL generation. Given the excellent mode quality of our fundamental the often employed hard-aperture selection of a central part of the beam does not improve the WL stability. If the mode deviates considerably from TEM_{00} it is, however, beneficial to select a region of uniform intensity distribution prior to WL generation.

A typical WL spectrum obtained at 1030 nm from the 3 mm sapphire plate is shown in Figure 3.1b. The spectral range can be extended beyond the 515 nm cut-off observed by choosing a different bulk material such as fused silica or CaF_2 ⁵⁵ with the latter yielding a WL spectrum down to 280 nm. Currently, however, materials with WLs blue shifted with respect to sapphire require translation to prevent damage accumulation thus resulting in a reduced WL stability. A different approach to generate bluer WLs is to up shift the seed frequency while relying on photostable sapphire. Representative spectra obtained at different seed frequencies are shown in Figure 3.1b. WLs down to 350 nm have recently been reported in 10 mm sapphire using a 515 nm seed.⁵⁶

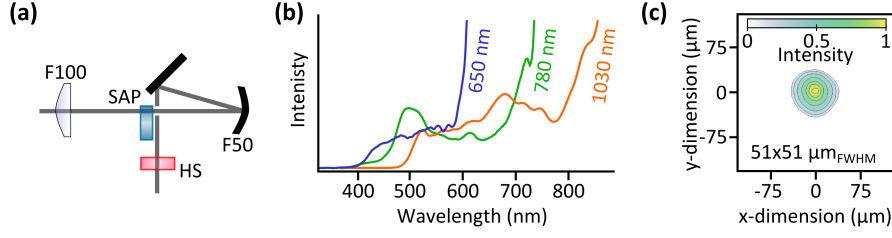


Figure 3.1: **Whitelight generation and properties.** (a) Schematic of a whitelight (WL) generation stage: SAP, 3 mm sapphire plate (Foctek Photonics); HS, 1 mm fused silica, 0° AOI, 1030 nm harmonics separator (EKSMA Optics). (b) WL spectra obtained at different seed wavelengths. (c) WL focusing properties at the sample position with a 200 mm focal length mirror.

The strong divergence of the WL generated calls for a relatively large reflection angle off the collimation mirror thus resulting in pronounced astigmatism. Owing the bandwidth (500-900 nm) of the WL, collimation by means of a lens would result in a drastically chirped WL and possibly add additional complications such as chromatic dispersion due to the limited spectral range of achromatic lenses. As an alternative one could evoke astigmatism free reflective collimation schemes⁵⁷ but examining the WL focusing properties at the sample position shows that our collimation approach ensures sufficient beam quality (Figure 3.1c).

Whitelight detection

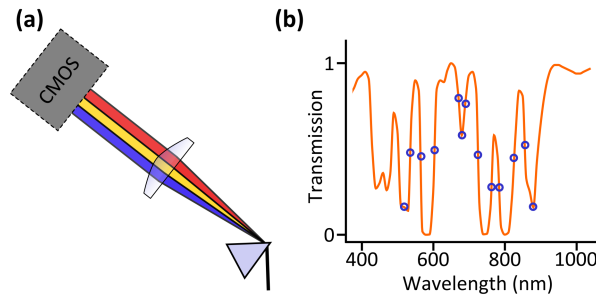


Figure 3.2: **Whitelight detection.** (a) Schematic of the prism based spectrometer. (b) FGB67 (Thorlabs) filter response (orange line) and positions commonly used in day-to-day spectrometer calibration (blue circles).

For detection of the WL probe pulses a home-built prism spectrometer consisting of a F2 prism (60° apex angle) in combination with a 50 mm NIR-

achromatic lens is used (Figure 3.2a). An ISG LightWise LW-ELIS-1024A-1394 CMOS line camera allows for single shot detection at 10 kHz with a full well capacity of 1 Me^- per pixel. At 10 kHz read out 10 adjacent pixels are averaged by a modulation transfer function thus increasing the full well capacity to 10 Me^- at the expense of spectral resolution. The 50 mm lens in combination with our WL results in focal spot dimensions of less than $10 \mu\text{m}^2$ and hence in a spectral resolution exceeding 60 cm^{-1} throughout the 500-900 nm detection window.

To reduce power losses in the intrinsically weak WL we omit the entrance slit in combination with an imaging system, in contrast to the commonly employed Czerny-Turner⁵⁸ spectrometer design. Spectral calibration is thus necessary prior to each measurement which is, however, easily achieved by recording the known filter response of a FGB67 filter (Thorlabs) as:

$$T(\lambda) = \frac{\text{WL}_{\text{filter}}}{\text{WL}_{\text{nofilter}}}, \quad (3.1)$$

with $T(\lambda)$ being the recorded filter transmission, $\text{WL}_{\text{filter}}$ and $\text{WL}_{\text{nofilter}}$ the WL spectra with and without the filter in place, respectively. The wavelength axis is obtained by choosing suitable reference points (Figure 3.2b) from the measured $T(\lambda)$ and fitting to the applicable dispersion equation of a prism based spectrograph.⁵⁹

Whitelight stability and referencing

A systematic WL stability optimisation is presented in Figure 3.3a. Here, we report the shot-to-shot stability, STSS_n as:

$$\text{STSS}_n = \frac{\text{WL}_{4n+0} + \text{WL}_{4n+1}}{\text{WL}_{4n+2} + \text{WL}_{4n+3}} - 1, \quad (3.2)$$

with WL_{4n+y} being the $4n+y$ th WL spectrum. We decided to divide pairs, rather than subsequent spectra, in order to avoid a non-zero baseline at 10 kHz read out of the LW-ELIS-1024A-1394 camera. By varying the focal point to sapphire front face position and the seed intensity we identify a region of enhanced stability ($\text{STSS}_n \approx 4.4 \cdot 10^{-4}$) around $2.5 \mu\text{J}$ when focusing 1 mm in front of the sapphire plate. This observation can be understood by considering that the correct balance between beam divergence and self-focusing will ultimately lead to very stable filament and thus WL generation. By screening different focal length lenses and materials we identify the 3 mm sapphire

in combination with a 100 mm focal length lens to perform best on our laser system. Once the optimum parameters are identified, day-to-day optimisation is achieved by monitoring the STSS while changing the lens-sapphire distance as well as the pulse intensity.

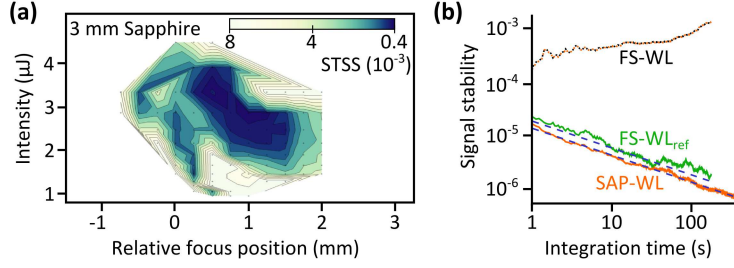


Figure 3.3: **Whitelight optimisation and stability.** (a) Shot-to-shot stability (STSS) as a function of seed intensity and focal point position with respect to the front face of a 3 mm sapphire plate obtained using a 200 fs pulse centered at 1030 nm with a 100 mm focal length lens. (b) WL stability in sapphire (orange), fused silica non-referenced (dotted) and referenced (green) as a function of integration time in comparison to shot-noise limited behavior (dashed).

It is possible to increase the stability, and hence sensitivity, of our STSS limit of $4.4 \cdot 10^{-4}$ by averaging multiple measurements:

$$\text{stability} \propto \frac{\sum_n \text{STSS}_n}{n}. \quad (3.3)$$

Under ideal conditions the highest achievable signal-to-noise ratio (SNR) is determined by the total number of electrons, and hence photons, collected by the detector. This sensitivity limit, called the *shot-noise-limit*, directly originates from the discrete nature of electric charge. For an experiment performed under ideal, shot-noise limited, conditions the SNR scales as:

$$\text{SNR} = \frac{nN}{\sqrt{nN}} = \sqrt{nN}, \quad (3.4)$$

with N being the number of electrons collected per laser shot n . Averaging increases the total amount of electrons collected and hence the SNR. Figure 3.3b shows a comparison of the sapphire WL stability as a function of integration time to the shot-noise limited behavior at a WL intensity of 550 ke^- per camera pixel. Our sapphire WL behaves shot-noise limited throughout the experiment with sensitivities below 10^{-6} . To further decrease this limit more electrons must be detected which would be possible by employing a more intense WL. Signal

magnitudes of VC are, however, on the order of 10^{-3} - 10^{-4} , a level easily reached using the WL probe.

To illustrate non shot-noise limited behavior we generate WL in a 3 mm fused silica plate which has to be constantly translated in order to prevent damage accumulation. The translation-induced noise results in a comparatively unstable WL (Figure 3.3b). Surprisingly, temporal integration does not result in any improvement of the signal stability. This behavior can be explained by so called catastrophic noise events⁶⁰ as for example the complete failure to generate WL at a particular point in time.

To nevertheless ensure close to shot-noise limited sensitivities one can reference the WL.⁶¹ We split the fused silica WL by means of a 50:50 beamsplitter and direct the pulse copies onto two separate spectrometers. The referenced fluctuations ($\text{STSS}_{ref,n}$) are computed as:

$$\text{STSS}_{ref,n} = \frac{\frac{\text{WL}^0_{4n+0} + \text{WL}^0_{4n+1}}{\text{WL}^0_{4n+2} + \text{WL}^0_{4n+3}}}{\frac{\text{WL}^1_{4n+0} + \text{WL}^1_{4n+1}}{\text{WL}^1_{4n+2} + \text{WL}^1_{4n+3}}} - 1, \quad (3.5)$$

with WL^0 and WL^1 being the two WL spectra detected. Comparison of the referenced STSS to shot-noise limited performance at 300 ke⁻ verifies that this approach is indeed capable of canceling most fluctuations.

Sub-10 fs pulses from a 515 nm pumped NOPA

To generate tunable sub-10 fs pulses in the NIR spectral range (650-980 nm) we construct a 515 nm pumped NOPA^{42,62,63} a schematic of which is shown in Figure 3.4a. Its design largely follows those reported for the established Ti:sapphire (800 nm) systems.^{64,65} We focus 3 μJ of fundamental using a 100 mm focal length lens into a 3 mm sapphire plate to generate the WL seed. Following recollimation with a 50 mm focal length curved mirror we hard aperture select the central 20% to avoid possible amplification artefacts introduced by the spectrally non-uniform rim of the WL. A 1 mm fused silica harmonic separator removes any residual fundamental from the WL that otherwise undergoes strong parametric amplification. The additional material chirps the WL to approximately match the temporal duration of the 515 nm pump pulse leading to an improved conversion efficiency.

The 515 nm pump (38 μJ) is temporally and spatially overlapped with the WL seed in a 2 mm BBO crystal ($\theta = 23.5^\circ$) at an internal angle of 2.5° (4.2°

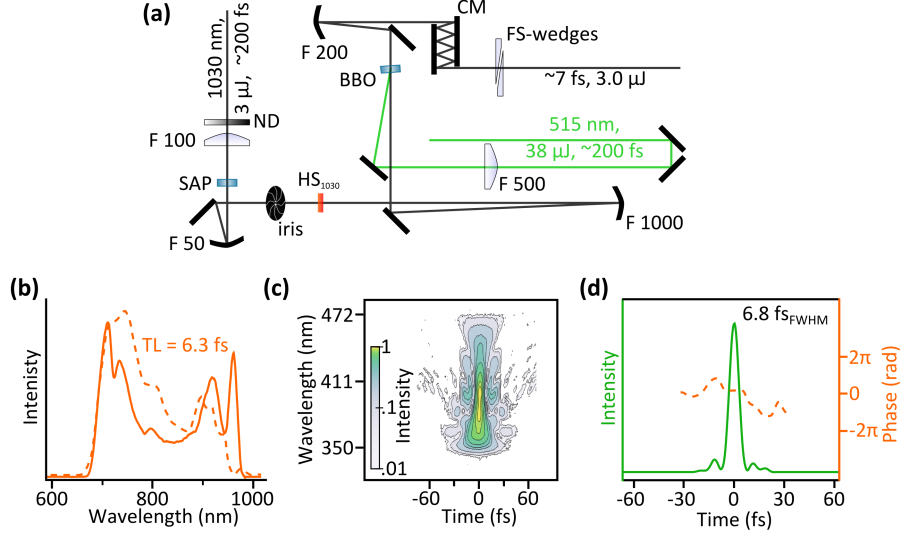


Figure 3.4: **Schematic and performance of a 515 nm pumped sub-10 fs NOPA.** (a) ND, variable neutral density filter; SAP, 3 mm sapphire plate (Foctek Photonics); HS₁₀₃₀, 1 mm fused silica, 0° AOI, 1030 nm harmonic separator (EKSMA Optics); BBO, β -barium borate 2.0 mm $\theta = 23.5^\circ$ type I (Foctek Photonics); CM, 680-980 nm chirped mirror compression GDD and TOD optimised (Layertec); FS-wedges, 2° apex angle fused silica prisms pair (Layertec). (b) Amplified output spectrum (solid) in comparison to the SHG-FROG retrieved spectrum (dashed). (c) SHG-FROG trace obtained after compression. (d) Temporal profile (solid) and phase (dashed) retrieved from (c).

external angle) in order to ensure broadband phase matching.⁴² The WL is focused 5.0 cm, the pump 8.5 cm before the BBO with the crystal to lens distances being 49.0 cm and 59.5 cm, respectively. We set the WL spot size at the crystal to being 2.5 times smaller than the pump by moving the collimation mirror after the WL generation stage. In this configuration the peak intensity is roughly 150 GW/cm², slightly lower than the often quoted 200 GW/cm² margin. The reduced peak intensity results in improved mode quality and pulse compressibility albeit at the cost of lower output power.

Following single-stage amplification we obtain pulses covering the 680-980 nm spectral range with intensities of 3 μJ corresponding to a conversion efficiency of 8%. A representative output spectrum is shown in Figure 3.4b. A combination of commercially available second and third order dispersion compensating mirrors (Layertec) and a pair of fused silica wedges, for fine adjustment of the phase, compresses the pulse to 6.8 fs, as verified by second-harmonic generation frequency resolved optical gating (SHG-FROG)⁶⁶ in a 10 μm BBO

(Figure 3.4c,d). The residual oscillatory phase is most likely caused by small sinusoidal modulations of the chirped mirrors phase response. We note a distinct lack of spectral components above 950 nm in the SHG-FROG retrieved spectrum (Figure 3.4b) which can be explained by the cut-off wavelength of the chirped mirrors at around 950 nm.

Sub-10 fs pulses from a 343 nm pumped NOPA

To generate broadband sub-10 fs pulses in the visible spectral region (480-650 nm), WL generated in sapphire with 1030 nm pumping is disadvantageous due to the spectral cut-off around 515 nm (Figure 3.1b). Measuring the spatial wavelength distribution reveals that the blue part of the spectrum is only present in the rim of the WL (Figure 3.5a). Following parametric amplification this spatial non-uniformity can result in severe space time coupling, which ultimately hampers the minimum achievable duration to around 12 fs. To generate shorter pulses it is necessary to blue shift the WL cut-off and hence the onset of spectral non-uniformity. As discussed earlier, this can be readily achieved by employing a different WL seed as shown in Figure 3.5b for the spatial distribution of a WL obtained by pumping a 3 mm sapphire plate at 780 nm.

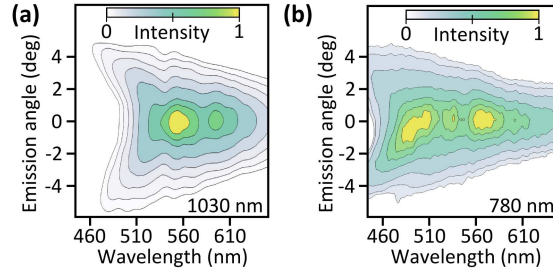


Figure 3.5: **Angular distribution of different whitelights.** (a) Angular wavelength distribution of a WL obtained at 1030 nm in a 3 mm sapphire plate. (b) Same as (a) but for a 780 nm seeded WL.

The necessity of generating the WL at a different wavelength results in the slightly more complex setup shown in Figure 3.6. A WL seed generation stage outputs $\sim 200 \text{ cm}^{-1}$ pulses centered at 780 nm that generate the blue shifted WL. Amplification with a 343 nm pump yields pulses tunable throughout the visible spectral region. As mentioned previously higher band gap materials could be used for the generation of a bluer WL. In this case, however, material

translation is necessary to prevent damage accumulation. We found it very difficult to generate a spectrally constant CaF_2 or fused silica WL at 10 kHz and almost impossible to maintain over the course of several hours. Shifting the WL seed to a different wavelength is the far more stable and easier to maintain alternative.

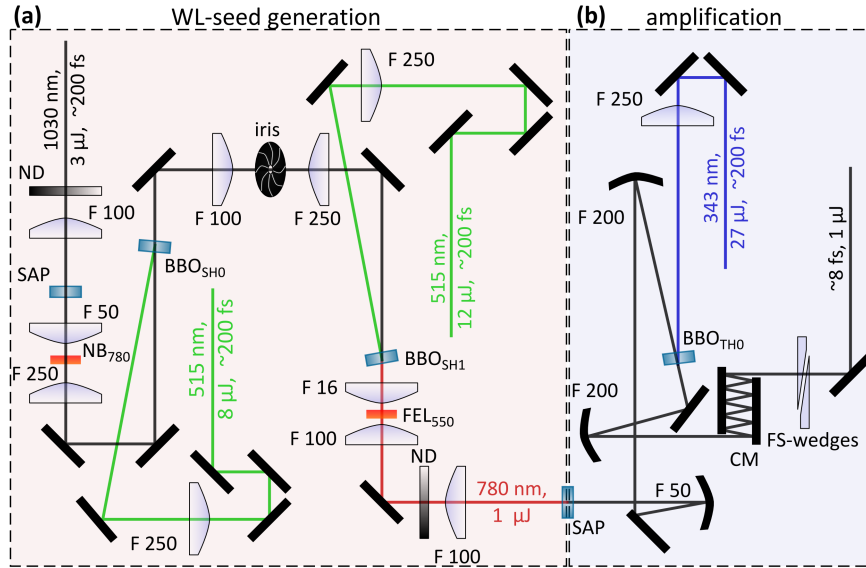


Figure 3.6: **Schematic of the 343 nm pumped sub-10 fs NOPA.** ND, variable neutral density filter; SAP, 3 mm sapphire plate (Foctek Photonics); NB₇₈₀, 780 nm dielectric 10 nm FWHM bandpass filter (FB780-10, Thorlabs); BBO_{SH0}, 2.0 mm $\theta = 23.5^\circ$ type I (Foctek Photonics); BBO_{SH1}, 2.0 mm $\theta = 23.5^\circ$ type I (Foctek Photonics); BBO_{TH0}, 2.0 mm $\theta = 37^\circ$ type I (Foctek Photonics); FEL₅₅₀, 550 nm dielectric longpass filter (FEL0550, Thorlabs); CM, 480-650 nm chirped mirror compression GDD and TOD optimised (Layertec); FS-wedges, 2° apex angle fused silica prism pair (Layertec).

Following recollimation of the WL generated by focusing 3 μJ of 1030 nm into a 3 mm sapphire using a 100 mm focal length lens we select 10 nm of its spectral bandwidth around 780 nm with a dielectric bandpass filter (Thorlabs). This preselection not only matches the WL seeds temporal duration to that of the 515 nm pump pulse (~ 200 fs) but furthermore avoids possible spectral detuning during NOPA alignment. It is thus possible to align the nominally complicated two-stage NOPA using only the output power as feedback. After spectral filtering pump and seed pulses are overlapped at an internal crossing angle of 0.5° (0.8° external angle) in a 2 mm BBO crystal ($\theta = 23.5^\circ$). The first amplification stage outputs 15 nJ pulses centered at 780 nm with crystal

to lens distances of 26.5 cm and 27.5 cm for the seed and the pump pulse, respectively. The seed focus position is adjusted to be 1.5 cm and the pump focus 2.5 cm in front of the BBO crystal face. The center of the recollimated output is hard aperture selected by means of an iris, which ultimately leads to a Gaussian mode profile after the second amplification stage. Seed and pump pulses are then focused into a second 2.0 mm thick BBO ($\theta = 23.5^\circ$), crossing at an internal angle of 0.5° (0.8° external angle). We set the pump focus position at 3.0 cm and the seed at 2.0 cm before the crystal with the BBO to lens distances being 28 cm and 25.5 cm, respectively.

Two-stage amplification yields collimated pulses ($1 \mu\text{J}$) centered at 780 nm with an elliptically Gaussian mode profile (2.5:1.3 mm at FWHM). The WL obtained at 780 nm is considerably blue-shifted with respect to 1030 nm WL (Figure 3.1b), moving the spectrally uniform part fully into the phase-matched amplification region (Figure 3.5b). A total of $20 \mu\text{J}$ of 515 nm would be sufficient to obtain output powers exceeding $1 \mu\text{J}$ in a single amplification stage. Our two-stage design, however, results in superior mode quality and stability as compared to a single stage NOPA, ultimately ensuring a long term stable 780 nm seeded WL.⁶⁷

The UV amplification stage (Figure 3.6b) closely resembles the 515 nm pumped femtosecond NOPA. $27 \mu\text{J}$ of 343 nm pump are overlapped with the WL, generated using 780 nm, at an internal angle of 4.2° (7.2° external angle) in a 2 mm BBO ($\theta = 37^\circ$ type I). Focusing optics to crystal distances are set to 29 cm and 28 cm for pump and seed, with the focal points being 4 cm and 3 cm before the BBO, respectively. The WL focusing conditions are fine-adjusted by moving the 50 mm focal length collimation mirror in the WL generation stage. In the configuration presented here only the center of the WL is amplified, avoiding the spectrally nonuniform regions at the rim of the WL. To avoid 2-photon induced long term damage accumulation⁵⁶ in the BBO it is necessary to reduced the peak intensity to $150 \text{ GW}/\text{cm}^2$ which allows for stable long-term operation over days.

Representative output spectra with intensities around $1 \mu\text{J}$ are shown in Figure 3.7a. A combination of second and third order dispersion compensating mirrors with a pair of fused silica wedge prisms allows us to compress pulses in the 485-640 nm spectral range to durations as short as 8.0 fs as verified by SHG-FROG in a 10 μm BBO (Figure 3.7b,c). Even though short pulses are desirable for many experimental application restricting the transform limit (TL) to ~ 10

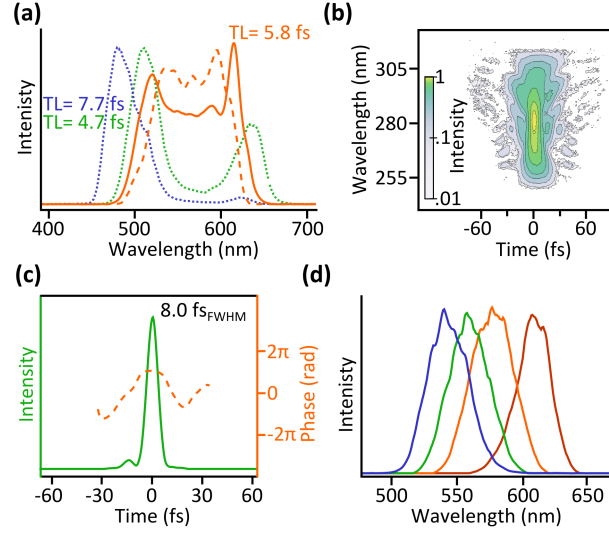


Figure 3.7: **Characterisation of the 343 nm pumped sub-10 fs NOPA.** (a) The pulse used for compression (solid) in comparison to the the SHG-FROG retrieved pulse spectrum and pulses showcasing the obtainable bandwidth in a 2 mm BBO (dotted). (b) SHG-FROG trace obtained after compression. (c) Temporal profile (solid) and phase (dashed) retrieved from (b). (d) Examples of pulse spectra obtained using a temporally longer WL seed generated in a 4 mm YAG plate.

fs drastically reduces the experimental hurdles associated with chirp management. Our pulses essentially cover the entire phase-matching bandwidth and spectral tuning is therefore merely possible by changing the pump-seed time delay as the 450-650 nm spectral range is temporally matched to the pump duration of 200 fs. Restricting the output bandwidth thus necessarily results in reduced output power. One way to circumvent this limitation is to introduce additional chirp into the WL prior to amplification which is ideally done by choosing a thicker WL generation medium. Figure 3.7d shows pulse spectra obtained by tuning the pump to WL time delay for a considerably more chirped WL generated in a 4 mm YAG plate. Comparable output powers as for broadband amplification are obtained but now at bandwidth supporting 10-12 fs pulses which are readily compressed by increasing the number of bounces on the chirped mirrors.

>150 fs pulses from a 515 nm pumped NOPA

Tunable pulses in the 630-950 nm spectral range, with bandwidth around 200 cm^{-1} and pulse duration of $\sim 200 \text{ fs}$ are obtained from a 515 nm pumped single

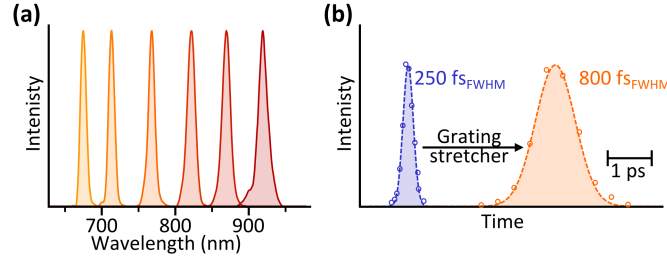


Figure 3.8: **Schematic and performance of a 515 nm pumped >150 fs NOPA.** (a) Representative spectra ^b. (b) Temporal profile of an 880 nm pulse before and after adding chirp by means of a grating stretcher.

stage NOPA. The design follows the one presented for the 515 nm pumped NOPA for 780 nm WL generation (Figure 3.6a). To allow for facile spectral tuning we chirp the WL with a 8 cm BK7 rod prior to amplification in a 4 mm BBO crystal. Figure 3.8a shows representative output spectra with typical pulse intensities of $\sim 8 \mu\text{J}$. UV pulses are accessible by second harmonic generation and depending on the experimental application a grating stretcher can be employed to chirp the output pulse (Figure 3.8b).

Pulse compression

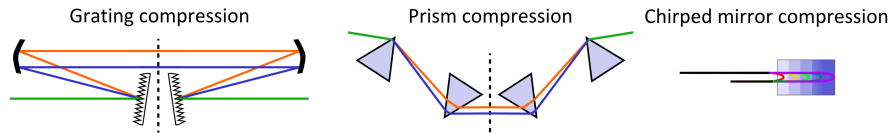


Figure 3.9: Commonly employed pulse compression schemes.

The most common pulse compression methods are shown in Figure 3.9. Owing to their large dispersion, grating based compression schemes⁶⁸ are often employed as they allow for the removal of large amounts of group delay dispersion (GDD). By changing the grating position with respect to the focusing mirror GDD can be added or removed. Even though it is possible to eliminate GDD contributions from an electric field, third order delay dispersion (TOD) is added. Compression of very short pulses is thus unfeasible by only using a grating stretcher. An alternative to grating based compression is the use of prisms.⁶⁹ A prism compressor allows for the removal of both GDD and TOD dispersion. The ratio of TOD and GDD elimination from a chirped pulse

does, however, not match the commonly encountered ratio induced by material dispersion. Prism compressors in the visible spectral region are thus limited to pulse durations of around 15 fs. Pulses down to 6 fs have been obtained by carefully balancing material dispersion with a combination of grating and prism based compression schemes.^{5,70}

The advancement of more refined pulse compression devices has drastically eased the experimental hurdles associated with obtaining sub-10 fs pulses. Both deformable mirrors as well as spatial light modulators (SLM), commonly placed in the Fourier plane of a grating or prism stretcher, have been employed in relatively simple compression schemes yielding pulses as short as 4 fs.^{71,72} Chirped mirrors⁷³ allow for the compensation of both GDD and TOD⁷⁴ by reflecting the pulse of interest off their surface.

For pulse compression in the 485-640 nm and 650-950 nm spectral range we rely on GDD and TOD compensating commercially available chirped mirrors (Layertec). We furthermore employ chirped mirror compression in combination with a 4f or 8f grating stretcher and an SLM in the Fourier plane, both for pulse compression and electric field synthesis. Pulses as blue as 450 nm are compressed to ~ 9 fs with a grating stretcher in combination with a 30 actuator deformable mirror.

Deformable mirror compression of the pump is achieved with a 600 grooves per millimeter grating and a 500 mm focal length focusing mirror in 4f configuration. The deformable mirror is placed in the Fourier plane and retro-reflects the beam at a slight angle. The collimated pulse leaving the 4f grating stretcher is characterised by SHG-FROG. A genetic algorithm maximises the second-harmonic intensity and commonly yields close to TL sub-10 fs pulses. For broadband WL compression we use a 150 grooves/mm grating. Due to the difficulties associated with obtaining a second-harmonic signal from the intrinsically weak WL we employ a combination of Spatial Encoded Arrangement for Temporal Analysis by Dispersing a Pair of Light E-fields (SEA-TADPOLE) and phase retrieval from a coherent artefact (CA) as explained in detail later.^{48,75} In brief, we record a differential absorbance map in 150 μm of BK7 with a compressed ~ 10 fs pump pulse. The probe pulse is the 0th diffraction order off the grating. This measurement allows us to retrieve the probe phase, as outlined in detail later. The residual phase of the WL leaving the grating stretcher is then determined by SEA-TADPOLE with the 0th order. Again, we employ a genetic algorithm for WL compression using the phase from SEA-TADPOLE

as feedback. Even though the measured phase can directly be applied to the deformable mirror we obtain better results with the genetic algorithm as we no longer rely on a, difficult to perform, wavelength calibration of the deformable mirror.

Electric field characterisation by SHG-FROG

Second-harmonic generation frequency resolved optical gating (SHG-FROG)^{66,76} is an easy to implement technique for the temporal characterisation of electric fields. Figure 3.10a shows a schematic of our SHG-FROG setup adapted from.⁷⁷ The pulse of interest is split into two identical copies, in our case by spatially cutting the beam in half using a half-mirror. Both pulses are then focused into a thin enough BBO crystal to allow for broadband phase-matching over the full second harmonic bandwidth.⁷⁸ The autocorrelation, or SHG-FROG trace, is obtained by varying the time delay between the pulse copies and detecting the background free second harmonic signal in spectrally dispersed fashion as:

$$I_{FROG}(\omega, \tau) = (E_{FROG}(\omega, \tau))^2 = \left| \int_{-\infty}^{\infty} E(t)E(t - \tau)e^{(-i\omega t)} dt \right|^2. \quad (3.6)$$

Retrieving the SHG-FROG-trace by means of an iterative algorithm (FROG 3.2.2. Swamp Optics) directly extracts the phase.⁷⁶ Even though SHG-FROG suffers from direction of time ambiguity as a result of it relying on a symmetric χ^2 interaction, it is never the less ideally suited for the characterisation of close to TL pulses.⁷⁹

An interferometric version of SHG-FROG, called iFROG, has recently been developed.⁸⁰ Here, a multipulse is generated, for example with the help of a SLM or a Michelson interferometer and the second harmonic signal is recorded as a function of inter pulse distance (Figure 3.10b) . A representative iFROG trace obtained for a 14.3 fs pulse centered at 557 nm is shown in Figure 3.10c. Due to the collinearity of the two beams the trace consists of multiple terms. These include the second harmonic signals of the two individual pulse copies, the SHG-FROG autocorrelation as well as multiple other contributions that show time dependent behavior.⁸⁰ To separate these components we apply a Fourier transformation and isolate the time independent part with a super-Gaussian window (Figure 3.10d). Inverse Fourier transformation followed by

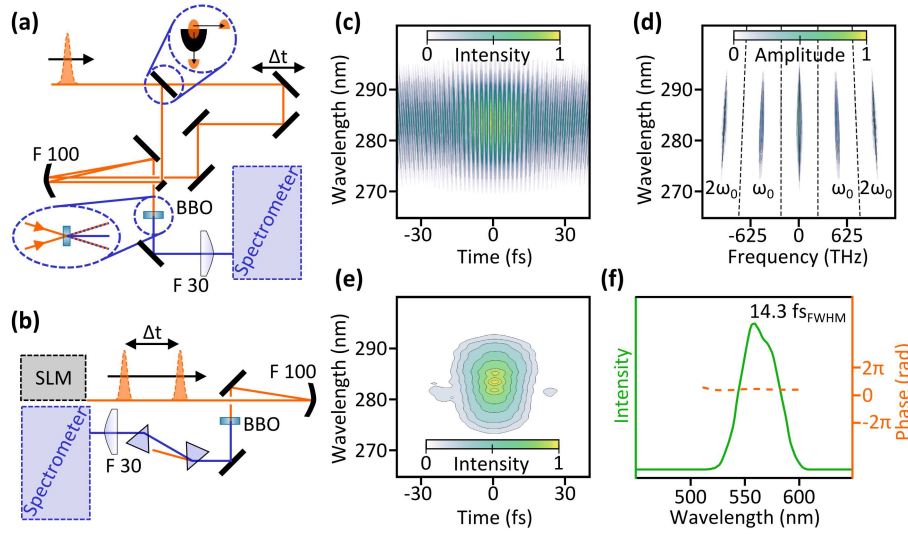


Figure 3.10: **Explanation of SHG-FROG and iFROG.** (a) Schematic of a SHG-FROG setup. BBO, 10 μm BBO supported on 2 mm UV fused silica (EKSMA Optics). (b) Schematic of a iFROG setup. BBO, 10 μm BBO supported on 2 mm UV fused silica (EKSMA Optics); SLM, spatial light modulator (Jenoptik AG). (c) Representative iFROG trace obtained for a ~ 14 fs pulse. (d) Fourier transformation of (c). (e) SHG-FROG trace obtained by Fourier filtering (c). (f) Temporal profile (solid) and phase (dashed) of the pulse.

subtraction of the constant second harmonic background yields a normal SHG-FROG trace which can be retrieved as above to fully characterise the electric field of interest (Figure 3.10e,f).

The advantage of iFROG over SHG-FROG is its compactness and the fact that possible pulse splitting artefacts, as for example imperfect beamsplitter balancing, are avoided. It is sufficient to place a BBO crystal at the position of the sample and record the second harmonic signal while generating a double pulse with the help of an SLM.

Electric field characterisation by SEA-TADPOLE

Spatial Encoded Arrangement for Temporal Analysis by Dispersing a Pair of Light E-fields (SEA-TADPOLE) is an interference based pulse characterisation technique.⁷⁵ An interferogram contains direct information on the phase difference between the interfering electric fields. Interferometric techniques have the distinct advantage over, for example SHG-FROG, that they do not rely on higher order processes and hence do not require high pulse intensities.⁸¹ Espe-

cially for complex, weak and temporally long pulses SEA-TADPOLE is a well suited technique.

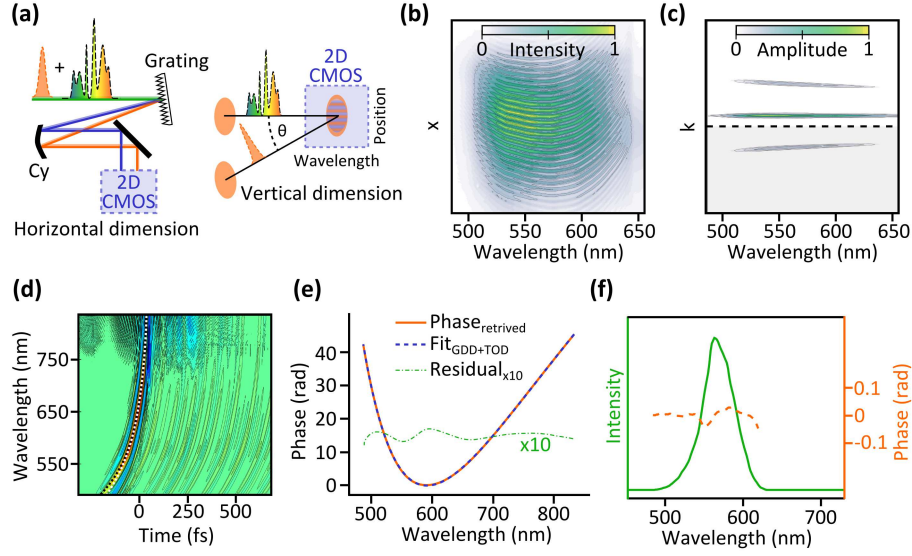


Figure 3.11: **SEA-TADPOLE based phase retrieval and reference generation.** (a) Schematic of the SEA-TADPOLE setup and beam overlap considerations. (b) 2D interferogram of an amplified pulse with a WL. (c) Absolute Fourier transformation of the 2D interferogram along the position dimension, the shaded area is used to extract phase information from the imaginary part. (d) Transient absorption map obtained using a 6 fs pulse centered at 800 nm for a 2:1 mixture of toluene and chloroform. Time zero obtained by retrieving the CA (black) and the phase of toluene and chloroform vibrational coherences (VCs) (white) are superimposed. (e) WL phase retrieved from the VCs in comparison to a fit using GDD and TOD only. (f) Spectrum (solid) and residual phase (dashed) retrieved by SHG-FROG for a pulse compressed using a SLM and phase information obtained with SEA-TADPOLE in combination with the WL phase from a CA.

A schematic of our SEA-TADPOLE setup is shown in Figure 3.11a. Two pulses, the "reference" and the "unknown" pulse enter the device and are spectrally dispersed in the horizontal dimension using a 150 grooves/mm grating. A 200 mm focal length cylindrical mirror (horizontal dimension) images the dispersed pulses onto a two-dimensional CMOS camera. In the vertical dimension the beams cross at a slight angle. If spatially and temporally overlapped onto the CMOS chip an interference pattern is observed in the vertical (position) dimension (Figure 3.11b). Relative alignment of the two dispersed beams in the wavelength dimension is easily performed by maximising the modulation depth of the interference. The intensity of this interferogram can be described by the following equation:^{75,82}

$$I(\lambda, x) = I_{ref}(\lambda) + I_{unk}(\lambda) + 2\sqrt{I_{ref}(\lambda)}\sqrt{I_{unk}(\lambda)} \cdot \cos(2kx \sin(\frac{\theta}{2}) + \phi_{unk}(\lambda) - \phi_{ref}(\lambda)), \quad (3.7)$$

with I_y being the respective pulse intensities, and θ the crossing angle between the beams. According to equation 3.7 it should be possible to isolate phase information by Fourier transformation along the position dimension:

$$\begin{aligned} \hat{f}(I(\lambda, x)) = I_{ref}(\lambda) + I_{unk}(\lambda) + E_{unk}(\lambda)E_{ref}^*(\lambda)\delta(k + \frac{4\pi}{\lambda}\sin(\frac{\theta}{2})) \\ + E_{unk}^*(\lambda)E_{ref}(\lambda)\delta(k - \frac{4\pi}{\lambda}\sin(\frac{\theta}{2})). \end{aligned} \quad (3.8)$$

The desired electric field information is now exclusively contained in the two sidebands (Figure 3.11c). After selecting one of the sidebands by multiplication with a square window function, inverse Fourier transformation directly reveals the spectral phase difference between the two pulses. As the interferogram was recorded in two dimensions, the SNR can be increased by averaging over the position axis.

To reveal the phase of the unknown pulse it is necessary to know the reference phase. Our approach is to use the WL probe pulse as a broadband reference. To illustrate the phase retrieval of the WL probe we record a transient absorption trace of a 2:1 mixture of toluene and chloroform (Figure 3.11d). The differential absorbance map shows a pronounced CA around time zero followed by coherent oscillations. The changing temporal position of the CA maximum is a direct manifestation of the WL chirp. Previously, it has been shown that time zero can be directly determined from the CA.⁴⁸ These CAs were, however, of much lower complexity. To show that the WL phase can be retrieved from our CA, we opt for a comparison with the time zero obtained from the coherent oscillations. In the limit of the excitation pulse being much shorter than the vibrational period under observation vibrational coherence generated in that mode behaves as either a sine or cosine function without additional phase.³² By employing a 6 fs excitation pulse centered at 800 nm and only considering toluene or chloroform frequencies up to 1211 cm⁻¹ we satisfy this delta pulse assumption. We extract time zero by determining the common point in time where all frequencies show zero-phase. The time zero from the CA is determined as the maximum of a Gaussian fit of the central part of the CA.

Figure 3.11d shows a comparison of the results obtained for the two approaches. We find excellent agreement of the time zero and hence WL phase over most of the spectral range. For wavelengths far away from the excitation pulse, however, we see slight discrepancies. These differences are most likely caused by the less well defined CA due to group velocity mismatch induced temporal broadening. We conclude that the CA retrieval method is suitable as long as phase information around the spectral region of the excitation pulse is desired.

For a non-amplified WL generated in a bulk material we do not expect non-trivial phase contributions. Comparison of the phase retrieved from the coherent oscillations to a fit using GDD and TOD thus provides an additional check for possible retrieval artefacts. Figure 3.11e shows that the deviations from our model are as small as ~ 0.2 rad.

We are now in a position to demonstrate that SEA-TADPOLE in combination with CA retrieval is indeed capable of correctly measuring the absolute phase of an electric field. Using a coarsely compressed 20 fs excitation pulse (9.5 fs TL) centered at 570 nm and a chirped WL probe we record a CA in 150 μm of BK7 glass. After retrieving the WL CA, and hence its phase, we measure the relative phase difference between the two pulses with SEA-TADPOLE. The absolute phase of the excitation pulse is computed as the difference between the two measurements. To test the result we apply the inverse phase, by means of an SLM, to the electric field of the excitation pulse. A perfectly compressed pulse should be obtained. A SHG-FROG measurement (Figure 3.11f) indeed verifies compression to the TL of 9.5 fs with residual phase contributions of less than 0.1 rad.

Amplitude and phase shaping with a spatial light modulator

An SLM^{83–86} allows for the, in principle, arbitrary modification of an initial waveform. An excellent introduction to pulse shaping by means of SLMs can be found elsewhere.⁸⁷ In brief, a liquid crystal SLM consists of two separately controllable masks each of which is composed of several pixels of nematic, that is birefringent, liquid crystals. The orientation of these crystals can be changed individually⁸⁸ by applying a voltage to each pixel of the liquid crystal mask. The changes in orientation result in a modification of the optical path due to the birefringent nature of the liquid crystal display. By employing two masks,

oriented perpendicular to each other, it is possible to control both the phase as well as the polarisation⁸⁹ of an electric field. If a polariser is placed behind the SLM polarisation control is translated into amplitude control. A dual-mask SLM equipped with polarisers thus allows for the independent control of phase and amplitude parameters of an electric field.

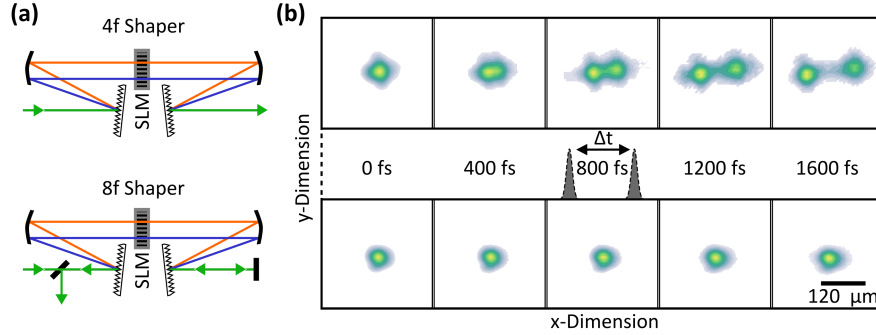


Figure 3.12: **Spatio-temporal coupling and spatial light modulators.** (a) Comparison of single pass (4f) and double pass (8f) grating based shaper setups. (b) Comparison between the pump focuses obtained for the 4f and 8f geometries with a 200 mm focal length mirror after generating a pulse pair using the SLM.

To address individual frequencies we disperse the incoming electric field by means of a grating and image it onto the mask of an SLM (Jenoptik SLM-S320d) in a so called 4f, zero-dispersion, grating stretcher (Figure 3.12a). By applying the desired phase and amplitude parameters to the SLM, arbitrary waveforms can be generated. As an unwanted side-effect, phase masks applied in the Fourier plane alter the focusing properties of the shaped pulse,^{90,91} an effect known as space-time coupling. Especially in experiments relying on non-changing pump-probe overlap this effect has to be minimised. One way to eliminate SLM induced space-time coupling is to operate the 4f-stretcher in a double pass, or 8f, geometry.⁹² Figure 3.12b shows a comparison of the pump focus measured at the sample position. We generate a double pulse with varying inter pulse delay to visualise the effect of space-time coupling in both the 4f and the 8f geometry. The strong changes in focusing conditions under 4f configuration are drastically reduced under 8f operation albeit not being completely suppressed.

3.2 Experimental spectroscopy

In the following section we will describe the main aspects of IVS, both experimentally as well as from a basic data processing perspective.

Transient absorption spectroscopy

The principle of broadband transient absorption (TA), or pump-probe, spectroscopy is illustrated in Figure 3.13a. A first pulse, called the pump pulse interacts with the sample of interest. The systems response is consecutively recorded with a second pulse, called the probe. In our case the probe is a broadband chirped WL and the pump a considerably more intense compressed ~ 10 fs pulse. Varying the time delay between the pump and the probe maps the temporal evolution of the system. By spectrally dispersing the probe pulse, information on the wavelength dependent changes following pump interaction are thus accessible. The pump-induced evolution manifests itself as small intensity changes of the WL spectrum. To increase the contrast of the measurement a differential transmission signal ($DTT(\lambda, \Delta t)$) is generated by computing the ratio of probe spectra recorded in the presence ($Pump_{ON}$) and absence ($Pump_{OFF}$) of the pump pulse.

$$DTT(\lambda, \Delta t) = \frac{Pump_{ON}}{Pump_{OFF}} - 1. \quad (3.9)$$

Experimentally, a mechanical chopper blocks every second pump pulse and the ratio of two consecutive probe pulses thus directly yields the differential signal. This detection scheme additionally takes advantage of the fact that subsequent laser pulses are correlated thus eliminating noise contributions from long-term power fluctuations.⁶⁰

If the pump pulse is tuned into resonance with an electronic transition, molecules are excited into higher lying electronic states and a mixture of excited and ground state molecules is generated. Without excitation only ground state population is present. If a differential measurement, in the presence and absence of the pump pulse, is performed three major signal contributions can be observed (Figure 3.13b). At the position of the ground state absorption spectrum more light is transmitted through the sample, as molecules have been removed by excitation into the higher lying electronic state. This phenomenon is known as ground state bleach (GSB). The excited molecules absorb light at a different wavelength resulting in diminished light transmission in the excited

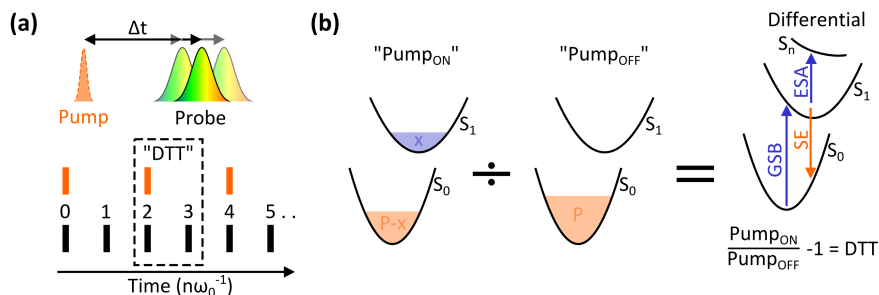


Figure 3.13: **Concept of transient absorption spectroscopy.** (a) Experimental implementation of transient absorption spectroscopy. (b) Common electronic signal contributions to the differential transmission (DTT): ESA, excited state absorption; GSB, ground state bleach; SE, stimulated emission.

state absorption (ESA) region. Stimulated emission (SE) from the excited electronic state is the third possible signal contribution leading to the detection of more light in the probe pulse.

Vibrational coherence

By using temporally short, and hence spectrally broad, pulses multiple vibrational eigenstates can be superimposed to generate vibrational coherence (VC).^{50,93} Depending on the resonance conditions of the pump pulse, VC can be generated impulsively on the ground electronic state (Figure 3.14a) or by excitation into a different electronic state (Figure 3.14b).^{13,32,50} As a result of the system no longer being in the eigenstate, a time dependent absorption or emission spectrum is observed (Figure 3.14c). The VC can be recorded in the form of oscillations by following the temporal evolution of the respective spectrum. A Fourier transformation reveals the vibrational frequency of the molecule in its respective nuclear coordinate.

Common vibrational frequencies for organic molecules are in the 200-3500 cm^{-1} frequency range, corresponding to vibrational periods ranging from 170-10 fs. Most spectral information is, however, concentrated in the so called fingerprint region ($<1600 \text{ cm}^{-1}$) with higher frequencies being dominated by C-H and O-H stretching modes. To extract spectral information from the VC recorded, it is often sufficient to ensure a high enough temporal resolution to resolve vibrational periods as short as 21 fs (1600 cm^{-1}). In a first approximation, the temporal resolution (t_{res}) of a TA experiment is determined by the durations of the pump and the probe pulses, in the limit of Gaussian pulses as:

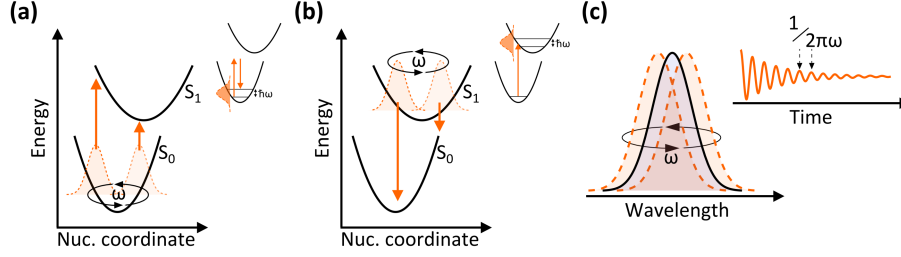


Figure 3.14: **Concept of vibrational coherence.** (a) Illustration of a nuclear wavepacket on the ground electronic state. (b) Illustration of a nuclear wavepacket on an excited electronic state generated by excitation from the ground electronic state. (c) Wavepacket motion manifesting itself in the form of a time dependent absorption spectrum.

$$t_{res} = \sqrt{\Delta\tau_{probe}^2 + \Delta\tau_{pump}^2}, \quad (3.10)$$

with $\Delta\tau_x$ being the respective pulse durations at full-width-half-maximum (FWHM). Even though the nominal duration of our WL is 300 fs the effective pulse duration in a TA experiment can be as short as 4 fs if detected in spectrally dispersed fashion with sufficiently high spectral resolution.^{48,94} A combination of chirped WL probe with a sub-10 fs pump pulse obtained from either the 515 nm or 343 nm NOPA presented earlier hence allows for temporal resolutions of around $\sqrt{4^2 + 10^2} = 10.8$ fs, sufficiently high to even detect high frequency C-H and O-H stretching frequencies above 3000 cm^{-1} .

Transient absorption experiments at high temporal resolution

After discussing some experimental considerations for recording both TA as well as the superimposed VC we will now outline a typical experiment. We spatially and temporally overlap a compressed pump (8.9 fs centered at 540 nm) with the chirped WL probe within a sample cell containing Rhodamine 101 dissolved in methanol. By stepping the time delay between pump and probe pulses, we record a spectrally resolved differential absorbance map ($\Delta OD(\lambda, \Delta t)$) by modulating the pump pulse with a mechanical chopper:

$$\Delta OD(\lambda, \Delta t) = -\text{Log}_{10} \left[\frac{Pump_{ON}}{Pump_{OFF}} \right], \quad (3.11)$$

with Pump_{ON} and Pump_{OFF} being WL spectra recorded in the presence and absence of the pump pulse, respectively. The differential absorbance map obtained in the 490 - 625 nm spectral region is shown in Figure 3.15a. The WL chirp manifests itself as a wavelength dependent time zero, rapidly followed by SE from the first excited electronic state of Rhodamine 101. As a result of the high temporal resolution VC is visible as oscillatory modulations of the transient signal.

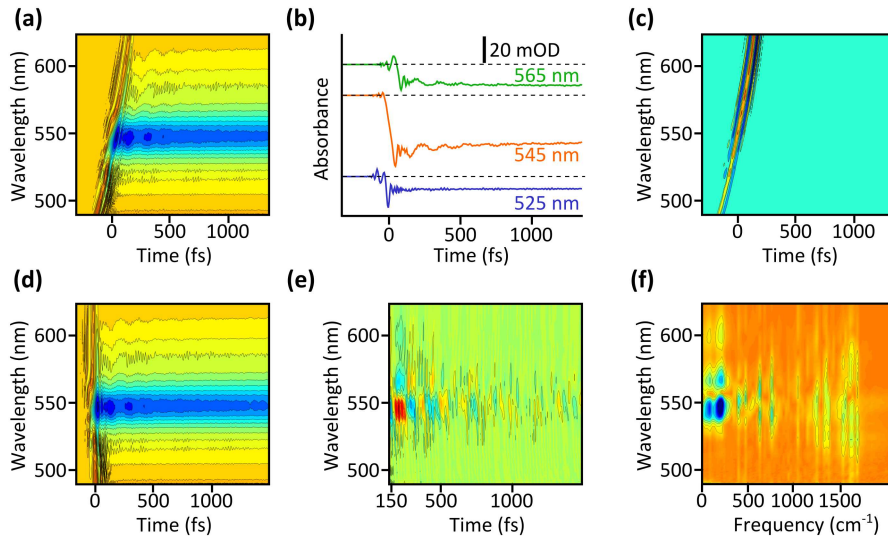


Figure 3.15: **Data processing, from raw data to Fourier spectra.** (a) Non time zero corrected differential absorbance map recorded for Rhodamine 101 ($\text{OD} = 0.7$) in methanol using a 8.9 fs pulse centered at 540 nm. The time axis is given with respect to the carrier frequency of the WL probe. (b) Spectral cuts highlighting the temporally ill-defined time zero point, the dashed lines indicate a signal level of 0 mOD. (c) non time zero corrected differential absorbance map recorded as (a) but on neat methanol. (d) Time zero corrected differential absorbance map obtained from (a) by interpolation. (e) Residual VC obtained after truncating (d) at $t = 120$ fs and removal of underlying electronic kinetics. (f) Fourier transformation of (e).

The first step in data processing is to correct for the wavelength dependent time zero as a result of the chirped WL. Retrieving the WL phase from the CA as explained previously can be difficult as the CA overlaps with the transient signal of Rhodamine 101 (Figure 3.15b) resulting in strongly varying CA shapes within our spectral detection window. To circumvent this problem we record a differential absorbance map for an off-resonant system prior to each resonant TA experiment. An ideal choice is the neat solvent, in this case methanol, which poses a comparable CA but without the complications arising from

the presence of other transient electronic signals (Figure 3.15c). By fitting the center part of the CA to a Gaussian function we obtain the wavelength dependent time zero, which allows for the correction of the chirped Rhodamine 101 map by interpolation onto a common time axes (Figure 3.15d).⁴⁸

The time zero corrected differential absorbance map can now be analysed. Electronic kinetics following photoexcitation can be described by a sum of exponentially decaying functions:

$$\text{fit}(t) = \sum_i a_i e^{\left(\frac{-t}{\tau_i}\right)}, \quad (3.12)$$

with t being the time axes, a_i the amplitude and τ_i the lifetime of the species i . Non-linear fitting to such a model function thus allows us to extract kinetic information. To describe the often complicated behavior around time zero an explicit CA model, signal rise times and temporal resolution contributions have to be included into the fitting model. Especially the CA shape can be non-trivial and no physically sensible analytical function is currently available for its description.⁴⁸ As we are mainly interested in the VC superimposed onto the electronic signal, rather than in ultrafast decay channels, we generally truncate the differential absorbance map after the CA and globally fit the map to the exponential model given above. By discarding all information before $t = 120$ fs and fitting to a single exponential decay, we can isolate the pure VC shown in Figure 3.15e. We note that most of the VC activity is concentrated around the SE signal as intuitively expected for VC modulating this electronic transition. A one-dimensional Fourier transformation on a wavelength by wavelength base reveals the spectral content of the VC (Figure 3.15f).

Chirped whitelight continuum probe

It has been theoretically shown, and experimentally verified, that high temporal resolution below 10 fs can be obtained with a chirped WL as long as spectrally resolved detection is used.^{48,94} No quantitative comparison between chirped and compressed probing has, however, been reported thus far.

To show that the temporal resolution is, in the limit of sufficiently high spectral resolution, independent of the WL probe duration we opt for broadband compression of our WL probe by means of a 4f-grating stretcher in combination with a deformable mirror.⁶⁴ We reduce the material in our WL to a minimum

and furthermore limit its bandwidth to the 510-840 nm spectral range. Following compression we obtain a 4.5 fs (4.2 fs TL) WL probe, as characterised by SEA-TADPOLE. Comparisons of the time-frequency representations of the WL with and without deformable mirror compression are shown in Figure 3.16a. We are, furthermore, able to change the WL duration by a factor of 30 by switching the deformable mirror thus allowing for an ideal comparison between chirped and compressed WL probing without any realignment being necessary between the TA experiments.

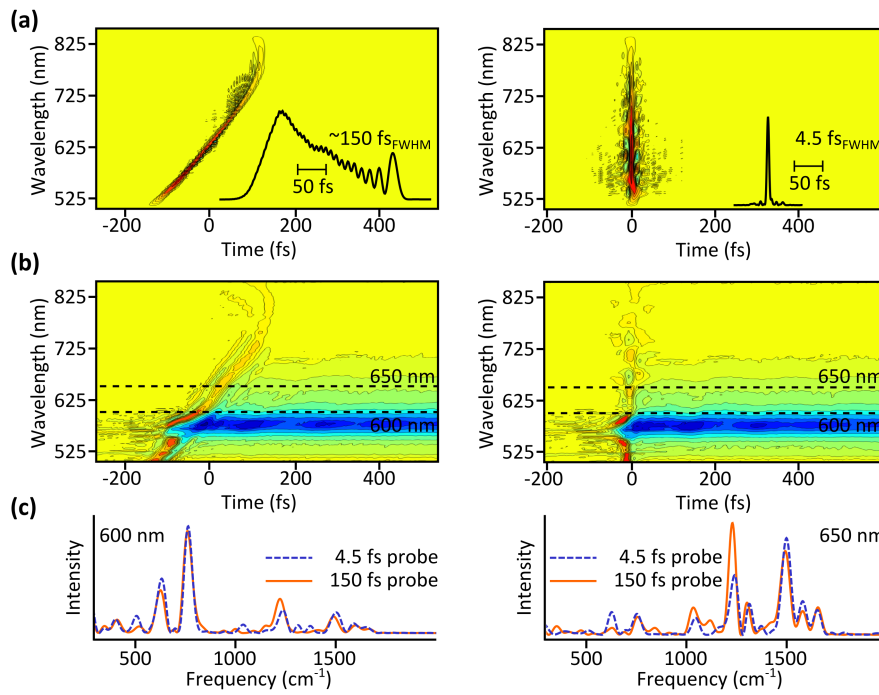


Figure 3.16: **Whitelight chirp and temporal resolution.** (a) Wigner representation of the WL probe before (left) and after (right) compression with a grating stretcher in combination with a deformable mirror. The electric fields were retrieved using SEA-TADPOLE. (b) Respective differential absorbance maps recorded for Rhodamine 101 in methanol using a 10 fs pump pulse and the chirped (left) and compressed (right) WL probe. (c) Comparison of the Fourier intensity spectra obtained for the compressed (dashed) and chirped (solid) WL probes. The spectra were generated from the VCs isolated by truncating the respective traces at $t = 100$ fs and subtracting the underlying electronic kinetics by means of an exponential fit.

A comparison of the differential absorbance maps obtained for the chirped and compressed WL is shown in Figure 3.16b. The pre time zero signal is a result of interference between pump photons with the WL probe. Even though this effect is present in every measurement it is especially pronounced here, a

result of the very low WL intensity. The two CAs exhibit very different shapes but closely resemble the respective WL time-frequency representations (Figure 3.16a), emphasising the different phase terms of the electric fields.

VC amplitudes strongly depend on the overall temporal resolution of an experiment. Fourier intensity spectra, with a square dependence on the temporal resolution, are thus an extremely sensitive probe for changes in the temporal resolution. Figure 3.16c highlights very good agreement for two representative Fourier intensity spectra obtained at 600 nm and 650 nm albeit a nominally 30 fold difference in WL probe duration. We thus conclude that the temporal resolution is not influenced by the duration of the probe pulse as long as sufficiently good spectral resolution is ensured in the detection. It is important to note that the best possible temporal resolution is determined by the TL of the probe pulse, irrespective of the spectral resolution.

Amplitude dependence of vibrational coherence

After having presented a general approach towards recording VC with a compressed pump and a chirped WL probe pulse we will now explore different factors that directly influence the VC amplitudes. Fine tuning these parameters allows us to establish ideal conditions for any experiment of interest.

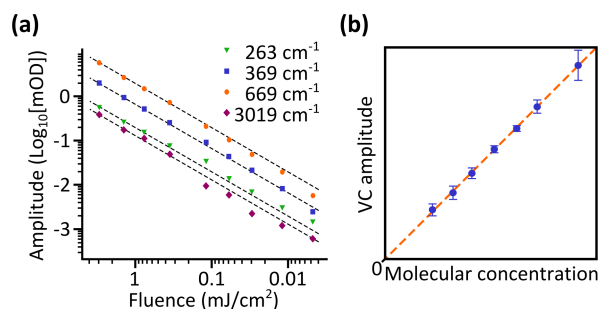


Figure 3.17: **Vibrational coherence magnitude.** (a) Log-Log plot of the pump-power dependence of the VC amplitude recorded in neat chloroform (dots). The dashed lines are guides to the eye for linear behavior. A 9.6 fs pulse centered at 520 nm in combination with a chirped WL probe are used. (b) Concentration dependence of VC amplitude obtained for Nile Blue in MeOH (dots) and linear fit (dashed line). The error bars show 95 percent confidence interval.

Two electric field interactions with the pump pulse are necessary to initiate VC and we thus expect a linear dependence of the VC amplitude on the

pump fluence.^{95,96} We experimentally verify this prediction by performing experiments on neat chloroform with pump intensities spanning more than three orders of magnitude and signal levels ranging from the mOD down to the nOD regime (Figure 3.17a). At a given pump fluence, the VC amplitudes should be proportional to the molecular concentration. Experiments on methanol solutions of Nile Blue, at different dilutions, allow us to verify the linear relationship (Figure 3.17b).

Above all, temporal resolution strongly influences VC amplitudes. As a rule of thumb sub-12 fs pump pulses ensure sufficient VC amplitudes in most TA experiments but shorter pulses can drastically boost the signal magnitudes. Figure 3.18a shows a comparison between the experimentally obtained relative VC amplitudes, as a function of pump duration, of the most prominent Raman active modes in acetonitrile in comparison to the theoretical predicted values. Especially high frequency modes exhibit rapid loss of amplitude with decreasing temporal resolution underlining why time domain observations of 3000 cm^{-1} oscillations are rarely reported in the literature. The 1381 cm^{-1} mode, being a good indicator for a high frequency VC within the fingerprint region, shows moderate decay with increasing pump duration and hence temporal resolution. Increasing the pump duration from 8 to 10, 12, 14, 16 fs results in a change of the relative VC amplitude of a 1500 cm^{-1} mode from 1 to 0.77, 0.56, 0.39, 0.25 of its original value at 8 fs.

As established previously, the WL duration does not influence the VC amplitude as long as sufficient spectral resolution is ensured. The theoretical TL of the probe pulse, however, directly influences the temporal resolution. We experimentally verify this prediction by spectrally filtering the probe pulse using a 4f-grating stretcher in combination with an adjustable hard aperture slit in the Fourier plane. Reducing the available bandwidth, and hence increasing the TL, of the probe reduces the VC amplitude (Figure 3.18b) even though the nominal probe duration decreases. We rationalise this finding by considering the following example: for a 10 fs pump pulse in combination with the broadband probe WL (TL ~ 4 fs) we compute a temporal resolution of $\sqrt{4^2 + 10^2} = 10.8$ fs (assuming Gaussian envelopes). Reducing the bandwidth to 10 fs TL results in 14.4 fs temporal resolution which in turn decreases the VC amplitudes. This finding has important implications, it shows that it is not only convenient to employ non-amplified, uncompressed, WL probes but their use positively impacts on the temporal resolution. Amplification of parts of the WL results

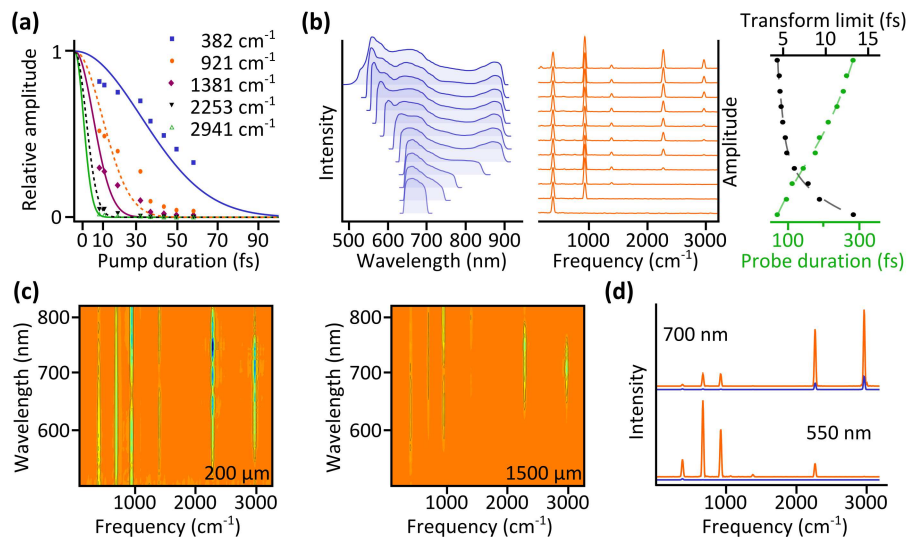


Figure 3.18: **Temporal resolution and vibrational coherence.** (a) Relative coherence amplitude (dots) as a function of pump duration measured for acetonitrile using a pump centered at 580 nm. The lines show the theoretically expected pump duration dependence. (b) Left, probe spectra obtained after narrowing the spectral bandwidth by means of a 4f-grating stretcher in combination with a hard aperture in the Fourier plane. Center, Fourier amplitude spectra obtained for acetonitrile by using the respective probe spectra (left) in combination with a 10 fs pump pulse centered at 570 nm. Right, TL and duration of the probe pulses. (c) Fourier amplitude maps normalised to the sample thickness recorded for acetonitrile at 200 μm (left) and 1500 μm (right) sample thickness using an 6.9 fs pulse centered at 750 nm. (d) Respective cuts at 700 nm and 550 nm for 200 μm (orange) and 1500 μm (blue) sample thickness.

in a nominal decrease in bandwidth and therefore, even after compression, reduced temporal resolution. In order to achieve the same temporal resolution (10.8 fs) with amplified, and compressed, pump and probe pulses one would have to employ two 7.5 fs pulses which is, from an experimental point of view, challenging.

Another important factor is the choice of flow cell thickness. While pump and probe pulses pass through the sample they accumulated chirp and, as a result, broaden temporally. As a consequence, a 12 fs TL pulse might yield larger VC amplitudes than an 8 fs TL pulse as the temporal broadening is far less pronounced in the former case due to the reduced bandwidth. Even more important are group-velocity mismatch (GVM) considerations, that is the effect of temporal walk-off between pump and probe pulses at different wavelength. When probing far from the excitation wavelength GVM can dom-

inate the overall temporal resolution, especially when employing $>200\ \mu\text{m}$ flow cells.

To illustrate the combination of both effects, we record Fourier intensity spectra of acetonitrile in 200 and 1500 μm thick flow cells using an 6.9 fs pump pulses centered at 750 nm. Fourier intensity maps, after normalisation to the flow cell thickness, are shown in Figure 3.18c. We opt for a normalisation to mimic an experiment with resonant molecules where the sample absorbance has to be kept at acceptable <1 OD levels to ensure a linear response of the sample as well as sufficient probe transmission. In this case an increase in flow cell thickness has to be accompanied by a decrease in sample concentration. The 200 μm map shows the known acetonitrile bands up to $2940\ \text{cm}^{-1}$ with slightly increased intensities at the position of the pump pulse. Increasing the flow cell thickness to 1500 μm drastically reduces the overall VC intensity especially outside of the pump region.

As no GVM contributions are present in the spectral region of the pump pulse the decrease is likely caused by deterioration of temporal resolution due to the chirp accumulated while passing through the flow cell. Outside of the pump region the VC intensities are reduced due to the effect of GVM. The 1500 μm case highlights the dominance of GVM contributions to the overall temporal resolution. Most of the VC disappear, even for modes with frequencies as low as $1000\ \text{cm}^{-1}$. A comparison of spectra obtained at 550 nm and 700 nm for the 200 μm and 1500 μm flow cells emphasises this observation (Figure 3.18d).

Fourier transformation basics

Frequency information is most conveniently extracted from any recorded VC by applying a Fourier transformation. A very detailed description of Fourier transformation techniques, both theoretically as well as with respect to the application to experimental data can be found elsewhere.⁹⁷ VC is recorded using a finite amount of data points N which are spaced by certain time steps, the so called sampling interval, Δt . The sampling rate, or sampling frequency, (ν_s) is calculated as:

$$\nu_s = \frac{1}{\Delta t}. \quad (3.13)$$

When recoding VC the sampling rate should be chosen appropriately to avoid aliasing, that is, two different frequencies becoming indistinguishable af-

ter applying the fast Fourier transformation algorithm (FFT). The highest frequency that is still correctly described is determined by the Nyquist frequency (ν_{Nq}) which is half the sampling rate. If we record, for example, a VC trace using 5 fs steps ($\Delta t = 5$ fs) the Nyquist frequency, ν_{Nq} is:

$$\nu_{Nq} = \frac{\nu_s}{2} = \frac{1}{2\Delta t} = 3335.64 \text{ cm}^{-1}. \quad (3.14)$$

A 2000 cm^{-1} VC would appear at the correct frequency after FFT. If the frequency was 4000 cm^{-1} , however, it would be "folded" around the Nyquist frequency and appear at:

$$3335.64 \text{ cm}^{-1} - (4000 - 3335.64) \text{ cm}^{-1} = 2671.28 \text{ cm}^{-1}. \quad (3.15)$$

Another important factor determined by the choice of experimental parameters is the frequency resolution ($d\nu$) which is given by the total acquisition time (T):

$$d\nu = \frac{1}{T} = \frac{1}{N\Delta t}. \quad (3.16)$$

Two bands with frequencies separated by less than the frequency resolution are indistinguishable. For two well separated bands it is, however, possible to determine their precise frequencies with accuracies exceeding the limit dictated by the frequency resolution.⁹⁸

From a practical perspective both the sampling interval as well as the total acquisition time have to be adapted to the experimental question. Additionally, noise contributions from pump scattering should be removed from the spectral region of interest. Visible frequencies are on the order of $\sim 20000 \text{ cm}^{-1}$ and interference of scattered pump photons with the probe will appear as discrete frequencies upon performing the FFT. The choice of an appropriate Nyquist frequency, however, allows us to move the interference-induced noise away from the frequency region of interest.

Discrete Fourier transformation basics

A Fourier transformation allows us to transform a function reversibly between the time and the frequency domain. For experimental data of finite length the discrete Fourier transformation (DFT) is often employed, which forms the basis of most FFT algorithms. The DFT assumes periodic sequences meaning that

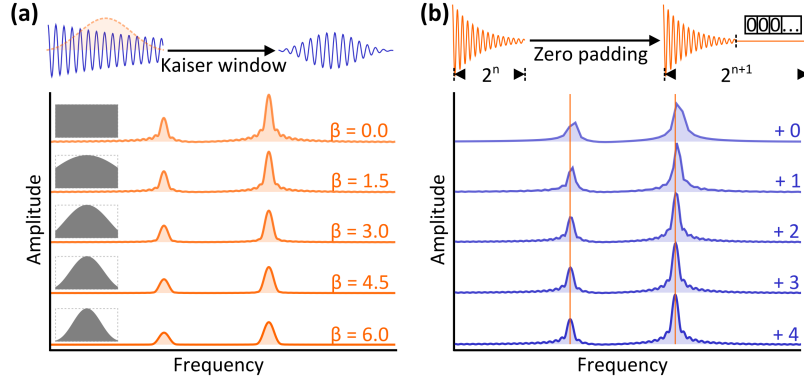


Figure 3.19: **Preparing vibrational coherences for a discrete Fourier transformation.** (a) The influence of windowing on the spectral band shape (orange) observed after discrete Fourier transformation illustrated for different Kaiser-Bessel windows (black). (b) Effect of zero padding illustrated for increasing padding lengths. The solid vertical lines indicate the correct frequency of the two bands.

if we acquired, for example, a sequence of $N = 256$ points (index: 0-255) index 256 and index 0 are assumed to be identical. Under experimental conditions this assumption is, however, rarely met thus leading to spectral leakage and ultimately to poor quality spectra. Application of a window function⁹⁹ to the data allows for the reduction of these undesired effects. Windowing can be understood as outlined in Figure 3.19a. Multiplication of the recorded VC with a window function reduces its beginning and end to values close to zero thus enforcing a periodic sequence. The reduction of spectral leakage is illustrated in Figure 3.19a for a series of different Kaiser-Bessel windows (KBW)^{99,100} defined as:

$$\text{KBW}(n) = \frac{I_0 \left(\beta \sqrt{1 - \left(\frac{2n}{N-1} - 1 \right)^2} \right)}{I_0(\beta)}, \quad (3.17)$$

with n being the n th index of the data point, N the total number of data points, I_0 the zeroth order modified Bessel function and β a parameter determining the width of the window. In the absence of a window ($\beta = 0$), we observe strong spectral leakage in the form of ringing. Increasing β , and hence the smoothness of the VC towards the edges of the recorded sequence, leads to a marked improvement of the spectral quality. Additionally, we observe broadening of the bands for increasing β , a manifestation of time-energy uncertainty. The window employed should thus always be adapted to the data set at hand as no universally applicable window function exists.

As discussed earlier, the Nyquist frequency determines the maximum resolvable frequency. A DFT of a data set consisting of N data points yields a spectrum with $N/2$ data points and a frequency spacing of $dn = \frac{1}{N\Delta t}$. This frequency spacing can be artificially decreased by zero padding (Figure 3.19b). Appending a vector consisting of zeros to the end of the data does not influence the Nyquist frequency as it is solely a function of the sampling interval ($\nu_{Nq} = \frac{1}{2\Delta t}$). The frequency spacing, however, is determined by both the Nyquist frequency as well as the length of the spectrum. By computationally increasing the length of the time trace, and hence the spectrum, we reduce the frequency spacing. Figure 3.19b shows the effect of zero padding on a spectrum obtained by applying a DFT to the sum of two sinusoids. Initially the bands appear at incorrect frequencies but shift as we increase the amount of zero padding. It is important to keep in mind that the spectral resolution of an experiment can not be improved by zero padding. Acquiring data over a longer time interval remains the only way of increasing the spectral resolution. Zero padding does, however, allows us to resolve frequencies if no adjacent bands are present in the spectrum.

An example of post processing for VC obtained for Rhodamine 101 dissolved in methanol is shown in Figure 3.20. Initially, we observe a poorly defined spectrum. Band shapes around 500 cm^{-1} , 800 cm^{-1} and 1300 cm^{-1} suggest that multiple frequencies might be present. By using zero padding we decrease the pixel spacing and are able to resolve two frequencies around 1300 cm^{-1} . Unfortunately, the ringing caused by spectral leakage is also better resolved, thus hampering our ability to judge the spectral content of the other bands. Application of a KBW reduces the effect of spectral leakage and ultimately resolve multiple bands around 500 cm^{-1} , 800 cm^{-1} and 1300 cm^{-1} . A thorough approach to zero padding in combination with windowing is thus a powerful tool that often facilitates the data analysis by providing spectra of the highest possible quality.

Electronic state assignment of vibrational coherences

VC originating from a particular electronic state temporally modulates its absorption spectrum.¹⁰¹ We should thus observe pronounced VC activity in the spectral region of the respective absorption spectrum. To test this hypothesis and to develop some guidelines on how to assign VC to its electronic state of

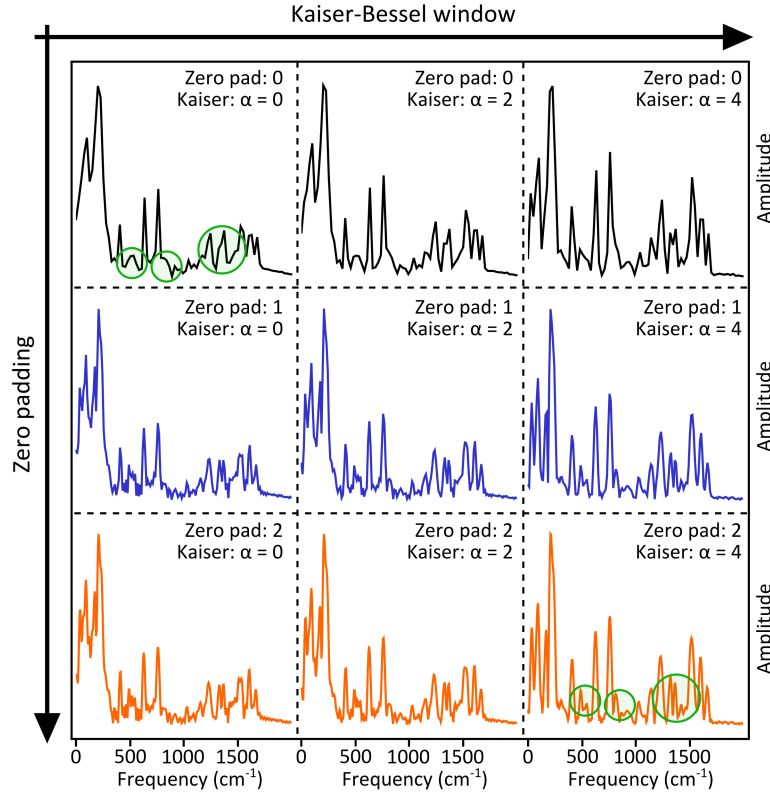


Figure 3.20: Influence of window size and zero padding on the final spectrum illustrated for a VC obtained for Rhodamine 101.

origin we perform two different experiments on Rhodamine 101 dissolved in methanol.

A 7.0 fs pulse centered at 790 nm, and hence completely off-resonant with the $S_1 \leftarrow S_0$ transition of Rhodamine 101, interacts with the sample but does not generate any excited electronic state population. VC in both methanol and the ground electronic state of Rhodamin 101 are, however, impulsively excited. By following the VC evolution as a function of pump-probe delay we obtain a differential absorbance map that, after time zero correction, removal of possible electronic contributions and Fourier transformation yields the Fourier intensity map shown in Figure 3.21a. A comparison of the wavelength dependent intensity distributions of the major bands shows a concentration of VC activity around the ground state absorption spectrum. For individual frequencies we observe intensity minima at wavelengths slightly red shifted with respect to the absorption maximum of Rhodamine 101.

These observations can be explained by revisiting the picture of a tempo-

rally evolving absorption spectrum introduced earlier. In the region of a large absorption spectrum gradient we expect strong, at the absorption maximum where the gradient is small negligible, VC activity.¹⁰¹ Different minima positions are present for individual frequencies which is most likely a manifestations of mode specific absorption spectra. The spectral red shift with respect to the absorption maximum for essentially all frequencies is caused by the VC formation. A superposition of multiple vibrational levels is necessarily energetically closer to the excited electronic state thus red shifting the wavelength necessary for the $S_1 \leftarrow S_0$ transition.

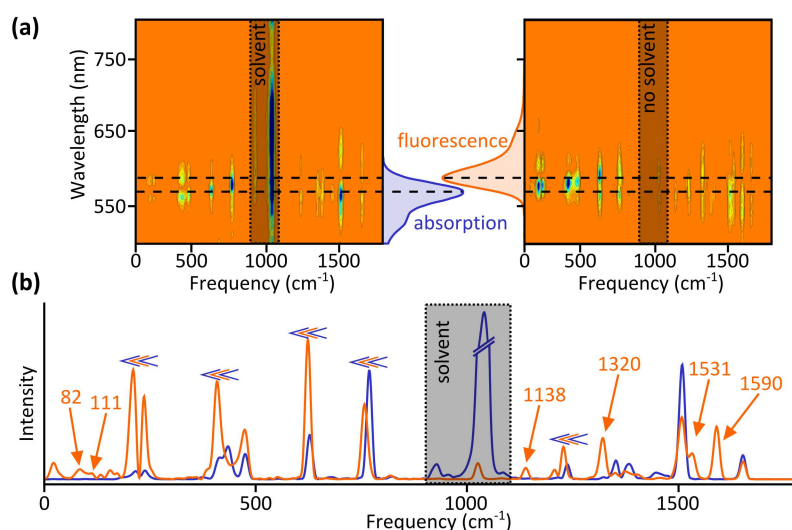


Figure 3.21: **Identifying excited state vibrational coherences.** (a) Left, Fourier intensity map obtained for Rhodamine 101 dissolved in methanol using an off-resonant pump pulse. Right, Fourier intensity map obtained for Rhodamine 101 dissolved in methanol using a fully-resonant pump pulse for excitation. (b) Spectra obtained by averaging the 530-650 nm spectral region under off-resonant (blue) and on-resonant (orange) conditions. Bands that appear (orange arrows) or shift (orange-blue triple arrows) under on-resonant experimental conditions are indicated.

Repeating the experiment with an on-resonant 8.9 fs pump centered at 540 nm yields the wavelength dependent VC activity shown in Figure 3.21a. In comparison to the Fourier intensity map obtained under off-resonant conditions we observe an even more pronounced red shift of the intensity minima, however, not beyond the maximum of the fluorescence spectrum of Rhodamine 101.

The red-shift in the off-resonant case was explained by superimposed ground electronic state vibrational levels which are energetically closer to the S_1 state

compared to a vibrationally cold system. For a SE, or fluorescence, transition the opposite is true. Exciting higher lying vibrational levels increases the S_0 - S_1 transition energy in agreement with the observed blue-shift of all intensity minima in comparison to the fluorescence spectrum. The strong enhancement of Rhodamine 101 over methanol VC furthermore hints towards the fact that we are indeed observing VC on S_1 . In an on-resonant experiment the VC generation is directly coupled to the electronic transition, a process far more probable than impulsive off-resonant generation of wavepackets.

The wavelength dependent Raman intensities are influenced by the specific pulses employed^{93,102,103} and our observation might thus solely be the result of the different pump pulses. Vibrational frequencies, on the other hand, are a function of the molecular system in its respective electronic state. Averaging the 530-650 nm spectral region of the Fourier intensity maps allows us to compare the spectral features obtained under on/off-resonant conditions (Figure 3.21b). We observe drastic differences between the two spectra. Almost all bands observed under off-resonant excitation conditions disappear from the spectrum and new features, as well as multiple bands of slightly shifted frequencies, emerge. Taken together, we see clear indication for the efficient generation of excited state VCs in Rhodamine 101 under resonant pumping.

The small Stokes shift of the fluorescence signal, in combination with the spectral similarity of the ground and excited electronic state VC, however, complicates the identification of excited electronic state VC. Combining experiments under on- and off-resonant pumping conditions allows us to assign most of the vibrational modes observed to the excited electronic state of Rhodamine 101. Without additional checks, the blind assignment of VC to an electronic state can, however, lead to drastic misinterpretations of experimental data.^{17,24}

Frequency estimates of vibrational coherences

A Fourier transformation preserves the phase information of an oscillation: $\cos(\omega t + \phi)$. The phase contribution, in turn, directly influences the line shape of the real and imaginary part of the FFT (Figure 3.22a). A purely absorptive real part is only present at zero phase, in all other cases dispersive, or negative, line shapes are observed. This problem is well known in NMR spectroscopy where the free induction decay is phase corrected prior to Fourier transformation to ensure a purely absorptive spectrum.¹⁰⁴ Even in the simplest case of VC generated under off-resonant conditions in neat solvent oscillations with 0

(cosine) and $\frac{3\pi}{2}$ (sine) phase are present.³² It is hence impossible to obtain a purely absorptive spectrum from the real part of the Fourier transformation and absolute or power spectra have to be used. These representations necessarily mix real and imaginary part and interference effects can occur.

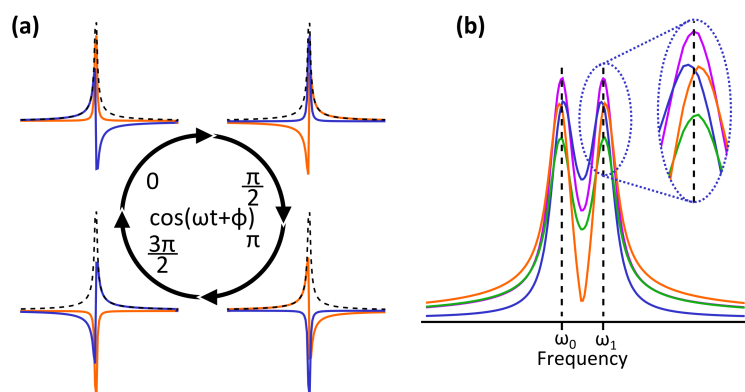


Figure 3.22: **Phase effects on line shapes.** (a) Real (orange) and imaginary (blue) part obtain after Fourier transformation of a cosinusoidal oscillation with added phase in comparison to the absolute value (dashed). (b) Fourier transformation of a sum of two oscillations at different relative phase. The dashed lines indicate the correct frequencies.

Figure 3.22b shows Fourier transformations obtained for a sum of two exponentially decaying oscillations which are close enough in frequency so that their bands partially overlap. Cycling the relative phase difference from 0- 2π results in shifting band maxima even though the frequencies are constant. Despite the effect not being dramatic, obtaining precise oscillation frequencies from the absolute of a Fourier transformation is often error prone. The reason for this is two-fold: firstly, the band maxima do no longer correspond to the oscillation frequency and secondly, the line shape is a function of the phase difference between oscillations and fitting the spectrum to, for example, a sum of Lorentzian functions is therefore impossible.

Spectra obtained from VC recorded for larger polyatomic systems, which can possess hundreds of degrees of freedom, are necessarily crowded and the interference induced artefacts can be quite severe, especially for temporally short VC traces. To showcase possible difficulties we simulated a VC consisting of 9 exponentially decaying oscillations with different phases, frequencies and lifetimes. We then generate an exponentially decaying window and multiply it with the simulated VC prior to Fourier transformation as outlined in Figure

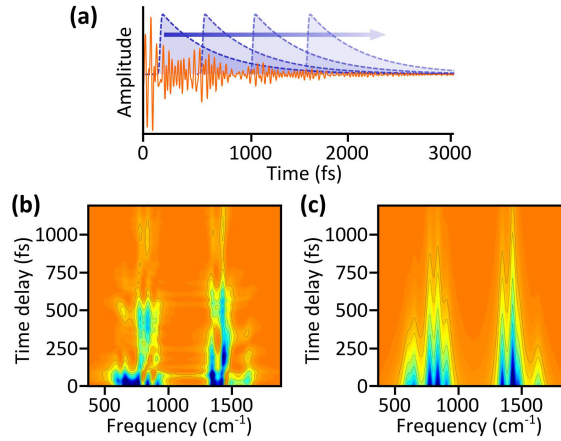


Figure 3.23: **Sliding window Fourier transform artefacts.** (a) Concept of sliding window Fourier transform (SWFT). (b) Time-frequency representation obtained after SWFT. (c) Time-frequency representation obtained by applying SWFT to each frequency individually. An exponentially decaying window (500 fs lifetime) with a 35 fs rise time was used to generate both maps from (a).

3.23a. Fourier intensity spectra, as a function of time delay between VC time zero and exponential window rise, yield a time-frequency representation of the VC as shown in Figure 3.23b, this approach is formally known as sliding window, or short-time, Fourier transform.¹⁰⁵ Drastic changes in both amplitudes as well as band position are observed. These dynamics are, however, solely a result of the changing relative phase terms of the 9 oscillations with respect to the exponential window onset. The frequencies remain constant and the correct time-frequency representation is shown in Figure 3.23c for comparison.

For congested spectra, it is thus necessary to extract the correct VC frequencies by some sort of fitting routine. As the line shape is no longer precisely defined in the absolute Fourier spectrum the fit must be performed before real and imaginary parts are merged. The most straight forward approach would be to fit the VC in the time domain by using a sum of cosine functions:

$$VC(t) = \sum_i a_i \cos(\omega_i t + \phi_i) e^{\left(\frac{-t}{\tau_i}\right)}, \quad (3.18)$$

with a_i being the amplitude, ω_i the frequency, ϕ_i the phase and τ_i the lifetime of VC i . Amplitude and phase can be obtained by linear optimisation, leaving two variables per VC for non-linear optimisation. A medium sized polyatomic posses 20-30 experimentally observable vibrational frequencies and

hence requires the non-linear optimisation of 40-60 parameters. A near-perfect starting guess is necessary to allow for fit convergence.

To obtain robust starting parameters for both lifetimes and frequencies we apply Linear Prediction Singular Value Decomposition (LPSVD).^{106,107} The starting values extracted from LPSVD are fed into a fitting routine implemented in Labview that non-linearly optimises the lifetimes and frequencies using a Levenberg-Marquardt Algorithm (LMA)^{108,109} while simultaneously linearly optimising the amplitude and phase terms by LU decomposition. LPSVD by itself yields very good frequency estimates but often introduces physically unrealistic behavior such as exponentially growing oscillations. The non-linear optimisation allows us to set constraints for the fitting parameters ultimately resulting in a physically correct description of the data.

All approaches presented assume exponentially decaying oscillations. Any dynamical change of the VC on the timescale of our measurements will therefore remain undetected. Time-frequency analysis might allow for the detection of changes but both sliding window Fourier transform as well as more sophisticated approaches such as wavelet analysis^{110,111} are, from our experience, extremely artefact prone if systems with multiple vibrational frequencies in the presence of measurement noise are analysed.

Temporal resolution correction

VC recorded in the time domain is necessarily convolved with the temporal resolution of the experiment.¹¹² As a result the band intensities obtained after Fourier transformation overemphasise low frequency with respect to high frequency contributions. If the precise intensities are important, for example to compare VC activity for different systems, it is necessary to correct for the effect of non-zero temporal resolution.

Using the absorption spectrum of the molecule under study, normalised to the optical density within the sample cell, and the excitation pulse spectrum, we compute the relative amount of VC generated at every point within the sample as the effective coherence generated (ECG). From the initial pump duration and the Sellmeier coefficients of the solvent, we compute the pulse duration after passing through the sample. Initial and final pulse durations in combination with the ECG allow for the calculation of a mean pump duration of the experiment. We estimate the temporal resolution from the probe and

the mean pump durations by either assuming Gaussian pulses or by directly convolving the two temporal profiles.

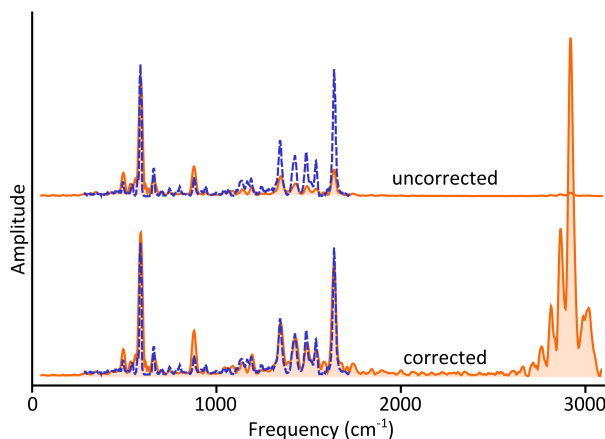


Figure 3.24: **Amplitude correction of Fourier spectra.** Top, Comparison of a resonance Raman spectrum of Nile Blue (blue, dashed) to the uncorrected amplitude spectrum obtained after Fourier transformation of VC obtained for Nile Blue using an off-resonant 10 fs pump centered at 800 nm averaged over the 510-700 nm spectral region (solid, orange). Bottom, comparison of a resonance Raman spectrum reproduced with permission from:¹¹³ Lawless, Mary K., Mathies, Richard A. *J. Chem. Phys.* **96**, 8037 (1992), <http://dx.doi.org/10.1063/1.462355>. Copyright 1992, AIP Publishing LLC with the temporal resolution corrected spectrum (orange, solid).

The time resolution obtained in this fashion has to be modified to account for spatial and temporal walk-off.^{41,114} The former is caused by the non-zero crossing angle between pump and probe pulses, the latter by the wavelength dependence of the refractive index. If small crossing angles are employed the effect of spatial walk-off is small and can be neglected. Temporal walk-off, on the other hand, can be extremely severe if systems are, for example, excited in the visible spectral region while NIR VC is probed.

To compute the temporal walk-off we calculate the group velocity mismatch between the pump carrier wavelength and the probe wavelength of interest. To computationally account for the temporal walk-off, we create a square function with a wavelength dependent temporal width determined by the group velocity mismatch. Multiplication of the square function with an exponential decay is necessary to account for the pump intensity depletion by absorption of photons within the sample. The wavelength dependent experimental time resolution is then approximated as the FWHM of the convolution of the pump/probe

cross-correlation with the exponentially decaying square function describing the temporal walk-off.

To validate our approach, we compare a raw with a temporal resolution corrected amplitude spectrum obtained for Nile Blue dissolved in methanol to a resonance Raman spectrum obtained at 531 nm taken from.¹¹³ After amplitude correction we find good agreement between the two spectra (Figure 3.24) thus underlying that temporal resolution effects in VC amplitudes can be accounted for. A distinct disadvantage of this approach is the drastic enhancement of noise at higher frequencies.

Chapter 4

Observing vibrational coherence on excited electronic states

Parts of this chapter have been adapted from the following publication: Liebel, M., Kukura, P., *J. Phys. Chem. Lett.* **2013**, 4, 1358-1364.⁵¹ Following our work, a similar paper was published by Kraack et. al.¹¹⁵ The data presented in their manuscript is in excellent agreement with my results thus validating our approach towards recording excited state Raman spectra. To allow for a sensible discussion only literature references published prior to the publication date (April 4, 2013) are considered in this chapter.

4.1 Introduction

The ability to follow reaction dynamics in real time has contributed tremendously to our understanding of photoinduced processes such as vision^{116,117} or light harvesting.^{118,119} Despite the great contributions of TA spectroscopy, its capabilities are limited to observing the temporal evolution of electronic absorption spectra. The changes in molecular structure underlying a particular transformation remain, however, largely unexplored. Vibrational spectroscopy is, in principle, capable of combining high temporal resolution with structural sensitivity but some limitations remain. Femtosecond infrared (IR) spectroscopy¹²⁰ relies on experimentally complex tunable IR sources. Compared to the visible spectral range the associated bandwidth is limited thus resulting in, comparatively, poor temporal resolution. Additionally, condensed phase applications are limited to spectral ranges determined by the solvent due to strong IR absorption. Frequency domain Raman techniques such as femtosecond stimulated Raman spectroscopy (FSRS),^{30,121} coherent anti-stokes Raman spectroscopy

(CARS)¹²² or time resolved resonance Raman spectroscopy (TR³)¹²³ are suitable for recording a systems evolution with temporal resolutions on the order of vibrational dephasing times. The initiation of VC can be timed with accuracies comparable to those of electronic spectroscopy and information on the structural evolution on these time scales is obtained.^{29,124,125} In the frequency domain, the full VC as well as all possible signal contributions, such as fluorescence, are necessarily averaged. This effect frequently leads to non-trivial backgrounds or interfering line shapes, especially when pulses in resonance with electronic transitions are present.^{126–128} The necessity to employ pre- or off-resonant pulses drastically reduces the possibility to increase the intrinsically weak Raman signal by resonance enhancement.

As a time domain analogue IVS, or ISRS (impulsive stimulated Raman spectroscopy)³² has been used to record vibrational activity in a variety of systems ranging from solvents⁵⁰ to proteins.¹⁷ Even though it has been demonstrated that IVS allows for the detection of high quality time domain Raman spectra spanning the full vibrational manifold¹⁸ its application to excited electronic states has been limited to the low frequency region of the vibrational spectrum.^{25,129}

We perform experiments on β -carotene¹³⁰ to demonstrate the capability of IVS in combination with a broadband, chirped, WL probe to record high quality Raman spectra in the time domain. β -carotene has been studied with numerous Raman techniques^{131–134} thus allowing for a direct comparison with the existing literature. Additionally, the highly up shifted C=C stretching mode in the S₁ state of β -carotene, around 1800 cm⁻¹, serves both as a benchmark for high temporal resolution as well as a background free marker band for a signal originating from the excited electronic state.¹³¹

Even though a C=C frequency shift of almost 300 cm⁻¹ might at first be surprising it is a direct consequence of the vibronic structure of β -carotene.^{131,135} Strong S₂-S₁ vibronic coupling¹³⁶ distorts the C_{2h} symmetry of the S₁ electronic state which allows for efficient S₁-S₀ coupling. Noguchi *et al.* tested this model by employing a variety of different solvents to tune the S₂-S₁ energy gap.¹³² Their results show that the C=C frequency directly correlates with the S₂-S₁ energy gap and hence the coupling efficiency to S₀.

4.2 Experimental and Results

Figure 4.1a shows a schematic of the three energetically lowest electronic singlet states of β -carotene. Optical excitation populates the second excited singlet state, S_2 , as the direct one-photon $S_1 \leftarrow S_0$ transition is symmetry forbidden. The initially populated S_2 state rapidly, within ~ 200 fs, decays into the first excited electronic state, which subsequently relaxes, within 8 ps, back to the ground electronic state.^{136–138}

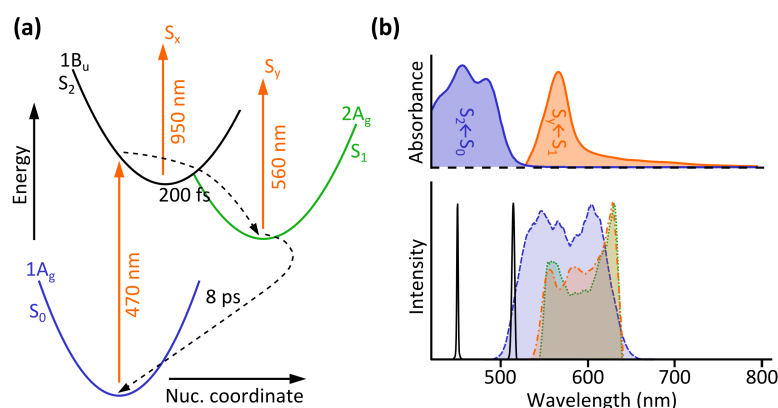


Figure 4.1: **Potential energy surfaces of β -carotene and pulses employed.** (a) Schematic of the three lowest lying electronic states of β -carotene including decay constants and one photon allowed transition energies. (b) $S_2 \leftarrow S_0$ (blue, solid) and $S_y \leftarrow S_1$ (orange, solid) absorption spectra of β -carotene dissolved in cyclohexane. The black, solid, pulses with 200 cm^{-1} bandwidth are used as actinic pumps in experiments on β -carotene dissolved in deuterated chloroform and cyclohexane (460 nm) or toluene (515 nm). The respective impulsive pump spectra are: deuterated chloroform (green, dotted), cyclohexane (orange, dashed-dotted) and toluene (blue, dashed).

Impulsive vibrational spectroscopy of β -carotene

To record the S_1 Raman spectrum of β -carotene dissolved in cyclohexane ($OD = 1$ in a $200\text{ }\mu\text{m}$ flow cell) with broadband-IVS (BB-IVS), we excite the system into the second excited electronic state by using an actinic pump pulse (200 nJ, 200 fs) centered at 450 nm (Figure 4.1b). After a waiting time of 2 ps, a mixture of vibrationally cold molecules in either S_1 or S_0 is present. We initiate VC in both excited, as well as ground electronic state molecules with a 12 fs impulsive pump (35 nJ) in resonance with the $S_y \leftarrow S_1$ excited state absorption transition. By recording differential absorption spectra as a function

of impulsive pump to WL probe delay, we follow the coherent evolution of the system. Similar experiments were performed for β -carotene dissolved in both deuterated chloroform and toluene pulse spectra of which are shown in Figure 4.1b for completeness.

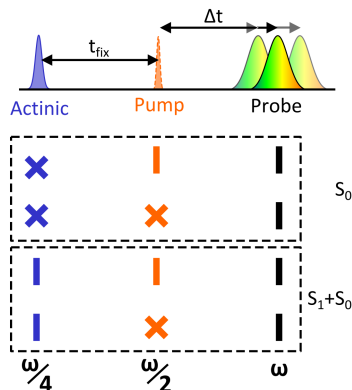


Figure 4.2: Pulses and chopping scheme employed for recording excited electronic state Raman spectra. Crosses represent blocked, lines unblocked beams.

The double chopping scheme outlined in Figure 4.2 allows us to perform two identical experiments but on different populations of the S_0 and the S_1 electronic states. If the actinic pulse is blocked a TA experiment on β -carotene molecules in the ground state only is recorded. In the presence of the actinic pulse both ground and excited state molecules interact with the impulsive pump and contribute to the signal.

Figure 4.3a shows the differential absorbance map recorded in the absence of the actinic pulse. Following the CA around time zero we observe the rise of a weak S_1 excited state absorption band centered around 560 nm. Even though the impulsive pulse is essentially off-resonant with the $S_2 \leftarrow S_0$ transition few β -carotene molecules are, nevertheless, one-photon excited into S_2 . Superimposed onto the electronic signal is strong VC activity throughout the entire spectral observation window. The same experiment is repeated in the presence of the actinic pulse, at an actinic to impulsive pump delay of 2 ps. Here, both S_0 as well as S_1 molecules interact with the impulsive pump. Following the CA around time zero we observe the bleach of S_1 absorption centered at 560 nm (Figure 4.3b), a result of the impulsive pump being resonant with the $S_y \leftarrow S_1$ ESA. The S_1 ESA partially recovers on a timescale of ~ 210 fs. Again, we observe VC superimposed onto the electronic signal throughout the differential absorbance map.

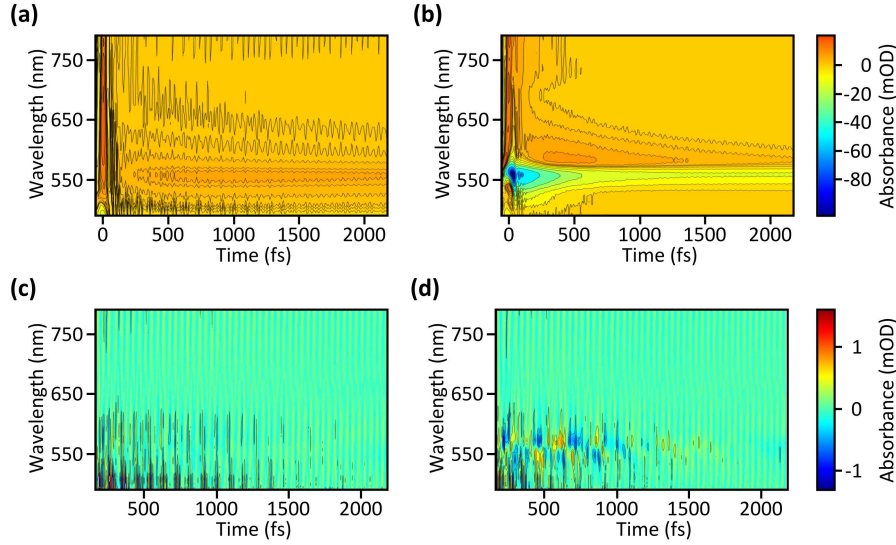


Figure 4.3: **Electronic kinetics and vibrational coherence of β -carotene in the presence and absence of the actinic pulse.** (a) Differential absorbance map obtained for β -carotene dissolved in cyclohexane after interaction with the impulsive pump in the absence of the actinic pulse. (b) As (a) but after generation of S_1 population by the actinic pulse. (c) Residual VC obtained for (a) after removal of the electronic kinetics. (d) Residual VC obtained for (b) after removal of the electronic kinetics.

To isolate the pure VC, we truncate the differential absorbance maps at a time delay of 170 fs and fit the underlying electronic kinetics to a sum of exponentially decaying functions. A comparison of the VC obtained in the two experiments reveals distinct differences in the oscillatory behavior (Figure 4.3c, d). In the actinic-off case VC is present over the full detection window, with slightly enhanced amplitudes in the spectral region of the impulsive pump. If S_1 population is present additional VC activity around the $S_y \leftarrow S_1$ ESA band with a phase jump at 560 nm appears. The spectral behavior of the VC is reminiscent of a time dependent S_1 absorption spectrum and hence the presence of S_1 coherence activity.

Frequency content of the vibrational coherence

We perform a Fourier transformation of the 520-660 nm spectral region to reveal the spectral content of the VC (Figure 4.4). A comparison with a Fourier intensity spectrum recorded under the same experimental conditions but on neat cyclohexane is shown for comparison. The most intense band in all spectra is a cyclohexane mode at 803 cm^{-1} , which explains the VC activity over the

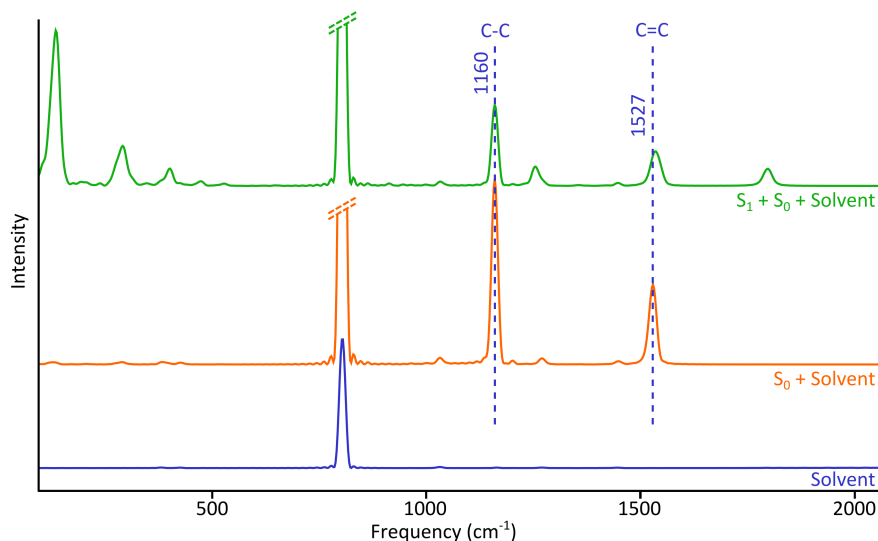


Figure 4.4: Comparison of the Fourier intensity spectra obtained by averaging the residual VC in the 520-660 nm spectral region for: Top, a mixture of solvent as well as β -carotene molecules in the ground and excited state; Center, solvent and ground state β -carotene molecules; Bottom, solvent only.

entire spectral range of the differential absorbance maps. The spectrum of the VC activity of β -carotene in its electronic ground state exhibits the well known C=C stretching band at 1527 cm^{-1} as well as the C-C stretching mode at 1160 cm^{-1} .^{18,139} If the actinic pulse, and hence S_1 population, is present the spectrum changes considerably. We observe a frequency shift of the 1527 cm^{-1} mode, additional bands in the frequency region below 500 cm^{-1} and at 1256 cm^{-1} as well as the previously reported S_1 marker band at 1798 cm^{-1} .¹³¹ Even though these frequencies originate from S_1 , contamination of the spectrum with both solvent (803 cm^{-1}) and β -carotene ground state modes (1160 cm^{-1}) is present. To isolate a clean excited state only Raman spectrum subtraction of these features is therefore necessary.

Subtraction in time and frequency domain Raman

Raman spectra recorded in the time or frequency domain often contain unwanted contributions such as solvent bands. To obtain the most representative spectrum of the molecule of interest these contaminations are removed by applying some sort of subtraction or filtering procedure.

Figure 4.5a illustrates the subtraction approach used for data acquired by a frequency domain technique such as spontaneous Raman or FSRS. The raw

data for a molecule dissolved in a solvent contains Raman signals of both species on top of a background caused by pump scattering and other contributions such as, for example, fluorescence. Background subtraction can be challenging, especially for fluorescent molecules,^{140,141} but satisfactory results are often obtained by modeling with, for example, a spline function, or experimentally with more sophisticated techniques such as shifted excitation Raman difference spectroscopy.^{142,143} Following background removal, a separately recorded solvent spectrum is, after amplitude scaling, subtracted to yield the clean solute only Raman spectrum.

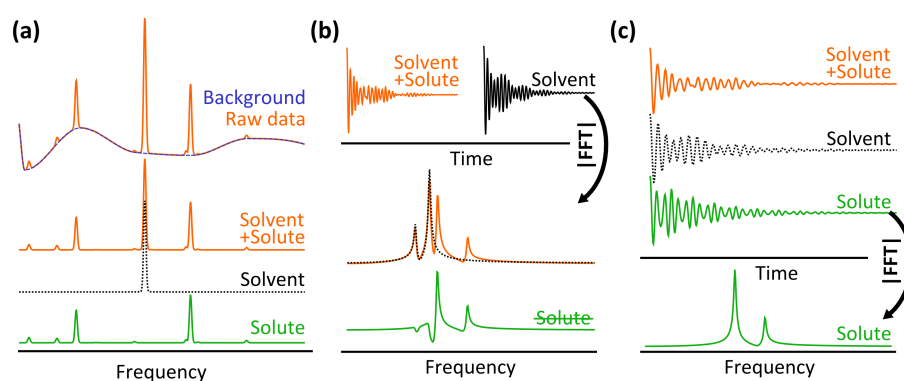


Figure 4.5: **Subtraction of solvent contributions from Raman spectra in time or frequency domain.** (a) Subtraction procedure employed in frequency domain Raman. (b) Only imperfect solvent removal is achieved when subtracting absolute spectra obtained from VC. (c) Subtraction of VC followed by Fourier transformation yields, in theory, a perfect solute spectrum.

For VC obtained in the time domain two different subtraction routes are, in principle, possible. Analogous to the frequency domain it is necessary to record data for the dissolved molecule of interest as well as VC of the neat solvent. Following Fourier transformation the two respective time domain Raman spectra are obtained. Note that the biggest error source in the frequency domain approach, the pronounced baseline, is absent in a time domain measurement as it only influences the DC term of the spectrum. Even off-resonantly generated VC exhibits a phase of either zero or $\pi/2$ and it is therefore not possible to use the real part of the Fourier transformation, if purely absorptive spectra are desired, but one is forced to rely on the absolute of the Fourier transformation of the spectrum in order to avoid dispersive line shapes (see Chapter 3). As discussed previously (Chapter 3) merging the real and imaginary parts causes line shape distortions due to the interference of different frequencies within

the spectrum. The line shape of the solvent bands in the solvent plus solute spectrum might thus be different from the pure solvent spectrum. A clean subtraction of the two absolute Fourier spectra is therefore impossible (Figure 4.5b).

This complication solely arises as phase information is lost upon computing the absolute spectrum. If the two VC are subtracted, clean solute only VC can be extracted. Computing the absolute Fourier transformation of the resulting VC yields the clean solute only time domain Raman spectrum (Figure 4.5c).

Automated subtraction algorithm for impulsive vibrational spectroscopy

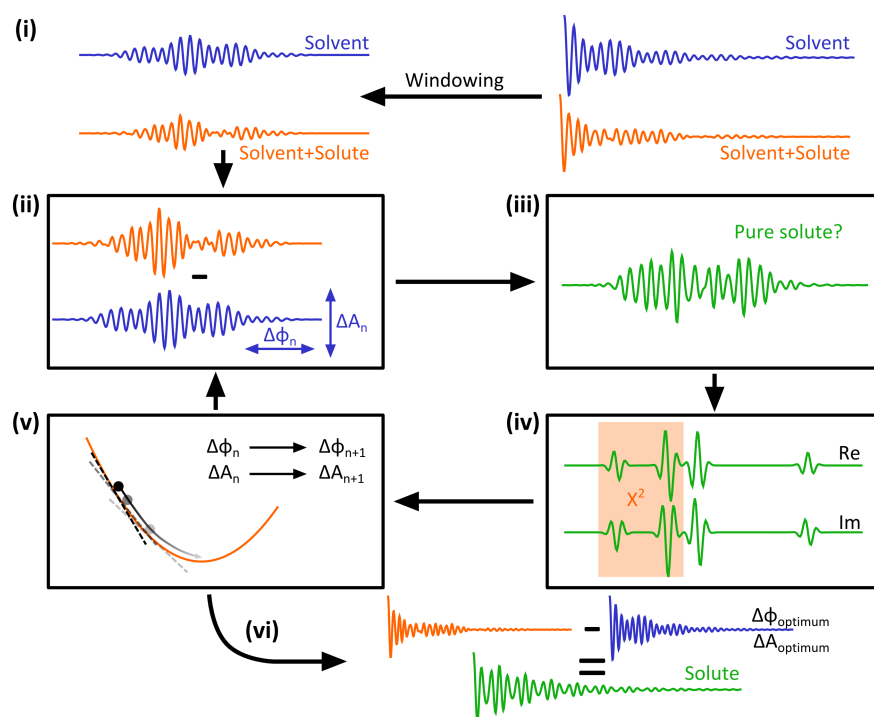


Figure 4.6: Time domain based subtraction algorithm.

The absence of baselines in Raman spectra recorded in the time domain allows for the implementation of an automated subtraction algorithm as outlined in Figure 4.6. Both VC recorded for solvent and solvent plus solute are windowed and fed into the optimisation algorithm alongside a starting guesses for amplitude scaling and phase shifts. Amplitude changes might, for example, occur as a result of absorption of pump photons by the solute molecules.

Less solvent VC is hence generated in the solvent plus solute experiment. As independent experiments are necessary to record both VC small drifts in the beam alignment often manifest themselves as changes in time zero hence calling for the phase, or time delay, correction term. Computationally, the phase correction can be implemented by interpolating the VC onto a different time axis or by, after Fourier transformation, multiplication with a linear imaginary function of the form:

$$e^{(i\omega\phi_{shift})}. \quad (4.1)$$

The scaled solvent VC is subtracted from the solvent plus solute VC resulting in a guess for pure solute VC. As the subtraction success cannot be evaluated from the VC, we perform a Fourier transformation. By selecting a spectral region with solvent activity the algorithm is able to compute the performance of the subtraction guess in a least square fashion. We use both real and imaginary part as feedback to facilitate fit convergence. The quality of the subtraction is evaluated by an LMA which computes improved amplitude scaling and phase correction terms for the following optimisation iteration. Once convergence is reached, the optimum phase and amplitude scaling factors are applied to the initial, non windowed, VC and a direct subtraction results in the clean isolation of pure solute only VC.

When processing experimental data the spectral range used as a feedback for fit convergence can tremendously affect the outcome of the subtraction. Great care has to be taken and results obtained for different regions should be compared to identify possible artefacts. Regions of closely spaced solvent and solute bands are generally not well suited as feedback. If VC maps as a function of time and wavelength have been recorded, it is advantageous to globally optimise the subtraction. To a first approximation, the amount of solvent VC generated depends on the pump power and using the entire VC map for optimisation is thus computationally more robust. Additionally, the temporal resolution between the solvent plus solute and the solvent only experiments might be different. This effect can be understood by considering a simple Beer-Lambert picture resulting in pump power depletion while the pulse is passing through a solution of electronically resonant molecules. As a result, more VC is generated at the front face of the sample than at the back. For the off-resonant experiment, on solvent alone, the same amount of VC is generated throughout the sample cell. An initially transform limited pulse accumulates

chirp while passing through the sample, that is, the temporal resolution becomes a function of the position in the sample. The combination of sample position dependent VC generation and chirp accumulation ultimately results in a difference in temporal resolution for the solvent and the solvent plus solute experiment. Correction for differences in temporal resolution can be included in the algorithm using a scaling term of the form:

$$\hat{f}(VC)e^{(t_{change}\omega^2)}, \quad (4.2)$$

with $\hat{f}(VC)$ being the Fourier transformation of the VC and t_{change} a model free scaling parameter. From our experience accounting for changes in temporal resolution can be very artefact prone and should only be considered if experiments were performed under drastic conditions such as $<500 \mu\text{m}$ thick flow cells in combination with high optical densities. In such a scenario a considerable change in temporal resolution between the experiments performed on solvent only and solvent plus solute is expected and the quality of the uncorrected subtraction might no longer be satisfactory.

Isolation of pure excited state contributions

The subtraction algorithm, and all technical considerations can be applied to more complicated problems such as the isolation of the S_1 spectrum of β -carotene from VC containing ground state, excited state and solvent VC. To achieve this, it is necessary to record three different data sets. A pure solvent VC, a VC containing solvent and ground state contributions as well as the solvent, ground and excited state VC.

A Fourier intensity map of the VC prior to any subtraction is shown in Figure 4.7a. The entire map is dominated by the previously observed highly Raman active 803 cm^{-1} mode of cyclohexane. Excited electronic state frequencies are, however, visible in the vicinity of the $S_y \leftarrow S_1$ ESA maximum. Some bands, such as the 1160 cm^{-1} or 1532 cm^{-1} contributions show enhanced intensities towards the spectral region of the S_0 absorption spectrum suggesting that they might, at least partially, originate from the ground electronic state. A spectral average over the 520-660 nm region confirms the dominance of solvent and some ground state features (Figure 4.7b)

Subtraction of the VC originating from cyclohexane results in a Fourier intensity map composed of frequencies from either the S_0 or S_1 state (Figure

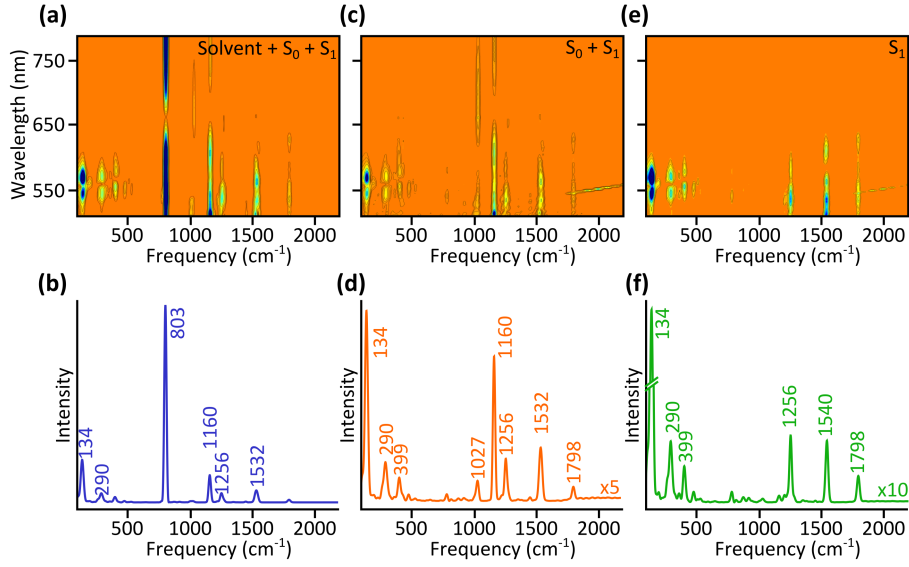


Figure 4.7: **Fourier intensity maps and spectra for β -carotene.** (a),(c),(e) Comparison of the Fourier intensity maps obtained for different degrees of S_0 and solvent subtraction. (b),(d),(f) Fourier intensity spectra obtained by averaging the 520 - 600 nm spectral region with major bands indicated.

4.7c,d). Most bands show intensity distributions reminiscent of the absorption spectrum of the first excited electronic state but ground state contributions remain, notably at 1027 cm^{-1} and 1160 cm^{-1} . The frequency shifting band in the $1800\text{--}2300\text{ cm}^{-1}$ spectral region around 550 nm is an artefact caused by interference of the impulsive pump and the probe pulses (see Chapter 3 for a discussion of pump-probe interference effects in Fourier transformations).

To isolate the pure S_1 spectrum, we first subtract the solvent contributions from the VC obtained in the experiment with blocked actinic pulse, resulting in S_0 only VC. These coherences are then subtracted from the VC obtained in the presence of the actinic pump minus the solvent VC to yield pure S_1 VC, a Fourier transformation of which is shown in Figure 4.7e. The wavelength averaged spectrum (520-600 nm) exhibits the expected, highly upshifted, C=C band at 1798 cm^{-1} , a C=C stretching mode at 1540 cm^{-1} and a C-C stretching contribution at 1256 cm^{-1} , several high intensity bands in the low frequency region at 134 , 290 and 399 cm^{-1} as well as multiple additional bands in the $400\text{--}1200\text{ cm}^{-1}$ spectral region (Figure 4.7f).

4.3 Discussion

The excited state Raman spectrum of β -carotene

Our observations are in excellent agreement, both in frequency as well as in intensity, with previously reported data obtained from a picosecond resonance Raman study on the S_1 state of β -carotene.¹⁴⁴ Some discrepancies with recent FSRS results are, however, apparent.¹³⁴ These difference are most likely due to the difficulties associated with ground state and baseline subtraction in frequency domain Raman spectroscopy. In the low frequency region, we observe numerous bands with the most intense being at 134, 290 and 399 cm^{-1} . None of these modes has been reported previously, most likely due to the experimental difficulties associated with accessing the region close to the Rayleigh band with a frequency domain technique. In the time domain, however, no such complications arise as long as the electronic kinetics are removed appropriately. The high frequency $>1000 \text{ cm}^{-1}$ spectral region of S_1 shows vibrational activity in modes comparable to that of the ground electronic state with the mode at 1256 cm^{-1} can be explained as an upshifted C-C stretching mode.¹⁴⁵ The *a priori* surprisingly strong activity in the low frequency spectral region can be explained by a distortion of the C_{2h} symmetry of the first excited electronic state due to strong vibronic coupling between S_2 and S_1 .¹³⁶ If a twisted chromophore is present the respective deltas for torsional modes should increase hence resulting in strongly enhanced Raman cross sections in the low frequency region of the vibrational spectrum.¹⁴⁶

The magnification of the 450-1300 cm^{-1} region, shown in Figure 4.8, highlights the spectral quality of Raman spectra recorded by BB-IVS. A slight disadvantage of such sensitivities is the accuracy with which the subtraction of ground state and solvent VC has to be performed. To verify the applicability of our subtraction algorithm, we opt for a comparison with an S_1 spectrum recorded in a different solvent.

Two bands at 783 and 815 cm^{-1} remain after subtraction of the ~ 1000 times larger 803 cm^{-1} band. Given the large intensity difference between these modes possible subtraction artefacts should be especially pronounced in this region. By choosing deuterated chloroform as a solvent we experimentally remove the cyclohexane contribution at 803 cm^{-1} . Repeating the experiment under, apart from the solvent, identical conditions reproduces the two bands in frequency, as

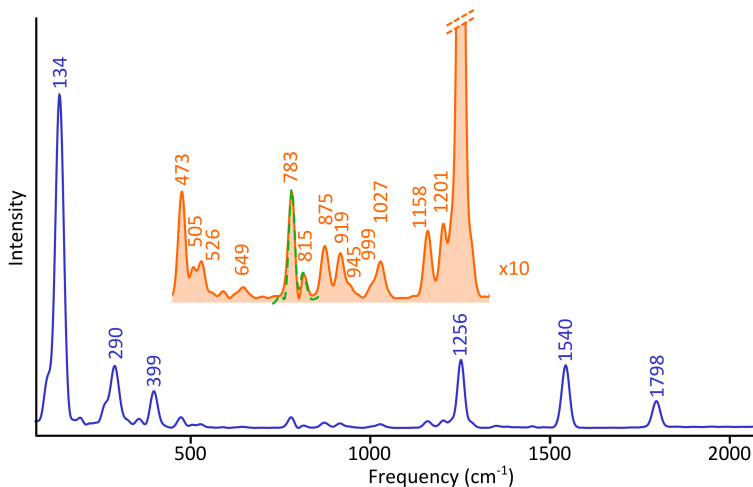


Figure 4.8: S_1 time domain Raman spectrum of β -carotene dissolved in cyclohexane (blue) and 10-fold magnification of the $450\text{--}1300\text{ cm}^{-1}$ spectral region (orange). A comparison of the spectral features obtained in the 803 cm^{-1} spectral region to data recorded using deuterated chloroform as a solvent is superimposed (black, dashed).

well as in line shape and intensity thus verifying that artefact free subtraction is indeed possible (Figure 4.8).

Time resolved vibrational kinetics of β -carotene

So far we presented a static S_1 Raman spectrum of β -carotene recorded in the time domain using BB-IVS. The actinic pump to impulsive pulse time delay was kept at a time delay of 2 ps throughout the experiment. To follow the temporal evolution of β -carotene, after photoexcitation, with vibrational sensitivity we record S_1 Raman spectra for different actinic to impulsive pump delays.^{133,147}

Figure 4.9 shows the S_1 spectra obtained for β -carotene dissolved in toluene ($OD = 1$, $200\text{ }\mu\text{m}$ flow cell) using an 8.2 fs (80 nJ, $70\times 67\text{ }\mu\text{m}$ focus at FWHM) impulsive pulse in combination with a 200 fs (520 nJ, $150\times 90\text{ }\mu\text{m}$ focus at FWHM) actinic pump centered at 515 nm (Figure 4.3b). The WL is focused to $55\times 55\text{ }\mu\text{m}$ (at FWHM). A higher actinic pump intensity, compared to the previous experiment, is necessary due to the unfavorable resonance conditions with the $S_2 \leftarrow S_0$ transition. By recording spectra at different actinic pump to impulsive pulse time delays we are able to follow the decay of the S_1 electronic state with vibrational sensitivity. The clean baseline before actinic to impulsive time zero, with no S_1 population present, furthermore demonstrates the sensitivity and selectivity of our approach.

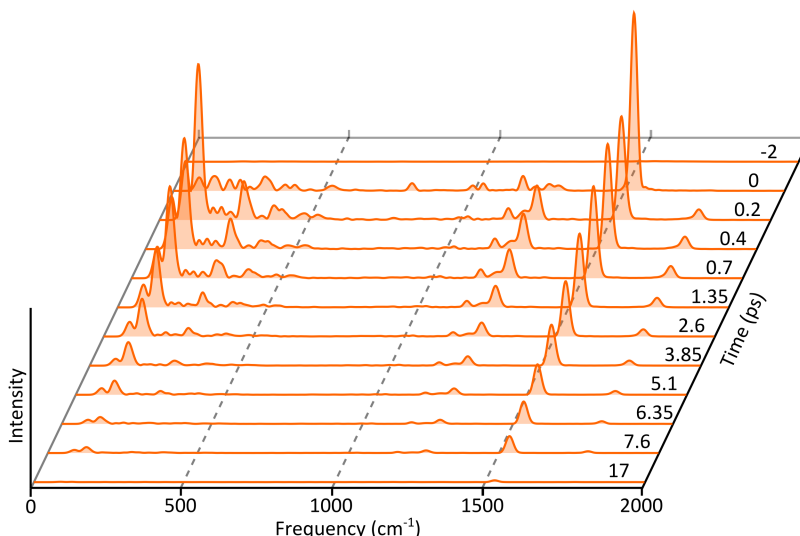


Figure 4.9: Following the decay of the S_1 state in β -carotene with vibrational sensitivity. Each spectrum is integrated for a total of 10 min (9 traces averaged per time point, 1.6 ps of VC used to generate each spectrum). The isolation of S_1 only contributions is performed by consecutive subtraction as described previously.

Notably, the spectrum recorded at time zero is markedly different from all other spectra even though 200 fs after photoexcitation a constant spectrum is obtained that decays concomitant with the electronic population of S_1 . This observation can be rationalised with the different deltas present in the Franck-Condon region. Directly after photoexcitation the strongest contribution to VC generation on S_2 is the $S_0 \leftarrow S_2$ transition due to the favourable resonance conditions with the impulsive pulse.¹³⁷ As the system has merely evolved we expect Raman activities comparable to those found in resonance with the $S_2 \leftarrow S_0$ transition. Indeed, the spectral intensities obtained by impulsive pumping at time zero closely resemble a resonance Raman spectrum of the ground electronic state with pronounced bands in the 1000, 1200 and 1500 cm^{-1} regions and little activity at lower frequencies ($<500 \text{ cm}^{-1}$). Due to the relatively long duration of the actinic pulse (200 fs) it is, however, not feasible to map the spectral evolution of the system over the first few tens of femtoseconds after photoexcitation.

4.4 Outlook and Conclusion

In summary, we developed a novel approach for obtaining excited state Raman spectra based on recording VC in the time domain with a chirped WL probe which we term broadband impulsive vibrational spectroscopy (BB-IVS). With respect to frequency domain techniques our approach does not suffer from complicated baselines. We can take full advantage of resonance enhancement, one of the most useful properties of Raman spectroscopy, by deliberately probing the electronic transitions of interest without suffering from fluorescence, non-linear backgrounds or line shape distortions. Our broadband detection scheme yields a clear wavelength dependence of the observed VC as well as their intensities, a feature that greatly simplifies the assignment of VC to its respective electronic state of origin.

We furthermore employed BB-IVS in a proof-of-principle experiment to record vibrational kinetics, a concept that will be explored in great detail in Chapter 7. Especially the drastically different S_1 spectrum around time zero suggests that the time domain approach might indeed be capable of probing the earliest events after photoexcitation if both actinic as well as impulsive pulses are temporally short. Even though the temporal resolution of any Raman technique is limited by either the decoherence or the integration time¹⁴⁸ a short impulsive pulse should, in principle, be able to encode the precise Raman cross sections within the Franck-Condon region into the VC. As long as these initial frequencies remain Raman active it should then be possible to extract the encoded information by recording the VC as presented here.

Chapter 5

Vibrational coherence of bacteriorhodopsin

Parts of this chapter have been adapted from the following publication: Liebel, M., Schnedermann, C., Bassolino, G., Taylor, G., Watts, A., Kukura, P., *Phys. Rev. Lett.* **2014**, 112, 238301¹⁴⁹ and are copyright (2014) by the American Physical Society. Most of the work presented was performed by myself with the exceptions of: Dr. Garrick Taylor provided the bacteriorhodopsin samples, Giovanni Bassolino provided the pma-RPSB chromophore and Christoph Schnedermann calculated the Raman spectra of pma-RPSB and nBu-RPSB and simulated the classical wavepacket trajectories.

5.1 Introduction

An ideal photochemical process uses all available photon energy to drive the desired chemical transformation. In reality, however, competition with alternative pathways limits specificity and efficiency. In terms of quantifying energy flow in molecules, ultrafast electronic spectroscopy is tremendously successful in recording kinetics on timescales longer than 50 fs^{116–118,150} and time resolved vibrational spectroscopy contributes information about the underlying structural transformations.^{120,121} Resonance Raman (RR) intensities provide complementary information by revealing the light-induced changes in atomic structure during the systems evolution out of the Franck-Condon (FC) region during the first few tens of femtoseconds after photoexcitation.^{146,151,152} Even for one of the best studied photochemical process, the isomerisation of the retinal chromophore,¹⁵³ the combination of these techniques fails to unravel the origin of

photochemical reactivity. The rate of isomerisation of the all-*trans* retinal protonated Schiff base (RPSB) in the proton pump bacteriorhodopsin (bR), found in the archaeon *Halobacterium halobium*,¹⁵⁴ compared to the solution environment^{118,155} does not explain the dramatically different quantum yields (Figure 5.1a).^{156,157} Indeed, isomerisation rates and yields in RPSBs seem to be largely uncorrelated.^{158,159}

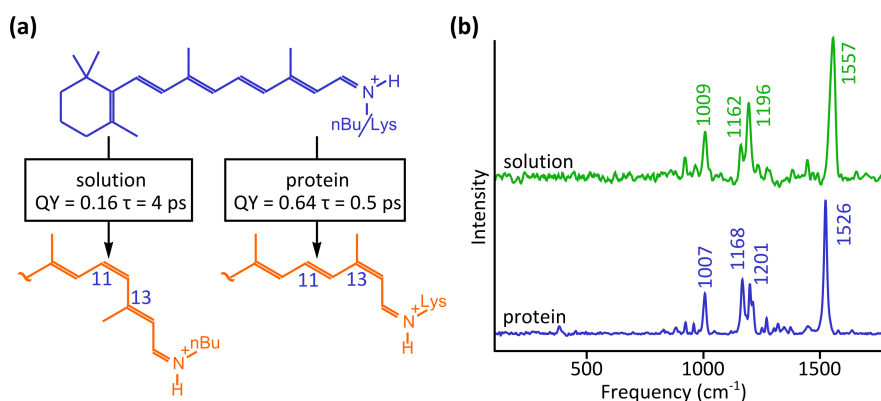


Figure 5.1: **Retinal protonated Schiff base photochemistry.** (a) The all-*trans* retinal protonated Schiff base (RPSB) chromophore shows drastically altered photo-physics depending on its environment. (b) Comparison of the pre-resonance Raman spectra recorded for nBu-RPSB in solution (top) and in the protein pocket of bacteriorhodopsin (bottom).

The RR intensities of RPSB in solution and in bR are essentially identical implying very similar starting geometries and initial structural evolution following photoexcitation (Figure 5.1b). If the nuclei for both systems respond in a similar fashion to photoexcitation and have a common starting structure, then the reactivity of the system must be determined outside of the FC region. Given that the excited state lifetime of RPSB in bR is considerably shorter than common vibrational dephasing times, its improved reactivity could be governed by vibrationally coherent activation of reactive pathways optimised within the protein pocket. Experimental verification of such coherent vibrational energy flow, how it differs in solution compared to the protein and to which degree it is related to differences in steady state photochemical reactivity, however, is lacking.^{160,161} Previous attempts to reveal such reactive nuclear wave packet evolution²⁴ have struggled either with interfering ground state signatures^{17,162} or insufficient temporal resolution revealing only low-frequency VC.¹⁵³

The absorption spectra of RPSBs are generally shifted towards the blue edge of the visible spectrum while excited state signatures, in the form of a SE transition, are found in the near infrared (NIR) spectral range. Conclusive observation of vibrationally coherent energy flow following photoexcitation thus calls for broadband probing windows in combination with high temporal resolution.¹⁶¹ Our methodology, relying on a chirped WL probe allows for the simultaneous observation of the GSB and SE bands in bR and, additionally, ensures sufficient temporal resolution to resolve VC with frequencies $>2000\text{ cm}^{-1}$ in the GVM dominated NIR region.

5.2 Experimental results

Bacteriorhodopsin sample

The bR membrane fragments are purified ^a according to standard procedures¹⁶³ and suspended in MilliQ water at an $\text{OD}_{568\text{nm}} = 0.45$ in a $500\text{ }\mu\text{m}$ flow cell. We opt for a relatively low OD and MilliQ rather than the more common buffer environment as a lower degree of aggregation, and hence scattering, is present in the former. MilliQ-suspended bR is still able to complete its full photocycle and shows the expected ground state Raman spectrum, even after being stored for weeks at 4° C . Irradiation with a fluorescent lamp equipped with both UV and NIR filters keeps the protein in its light adapted form throughout the experiment. To minimise flow induced shear we perform the TA experiments on RPSB in bR at a reduced laser repetition rate of 2 kHz . At this rate we are able to replenish the sample between consecutive laser shots without damaging the protein sample, even after several hours of experiment.

Impulsive vibrational spectroscopy of bacteriorhodopsin

To probe the vibrationally coherent energy flow, we excite RPSB in bR with an ultrashort visible pulse and generate VC in all FC active nuclear degrees of freedom that couple to the optical transition (Figure 5.2a).⁹³ VC generated on the ground electronic state oscillates about its equilibrium position, whereas on S_1 it rapidly moves out of the FC region towards a new stationary point (Figure 5.2b). At this local minimum, the backbone structure has evolved little

^abR purification and characterisation was performed by Dr. Garrick Taylor

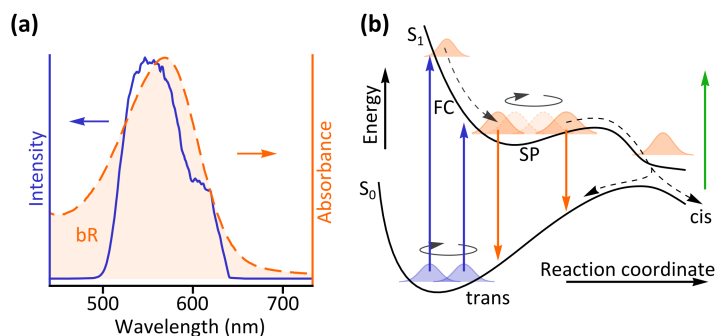


Figure 5.2: **Retinal protonated Schiff base potential energy surface and absorption spectrum.** (a) Absorption spectrum of bR (orange, dashed) and spectrum of the 9.6 fs excitation pulse (blue, solid). (b) Schematic of the potential energy surfaces (PES) of the S_0 and S_1 states of RPSB along the isomerisation coordinate. FC, Franck-Condon region; SP, stationary point.

along the isomerisation coordinate and experiences a barrier towards excited state decay and hence photoisomerisation.^{164,165}

A differential absorbance map recorded after photoexcitation of RPSB in bR with a 9.6 fs pulse is shown in Figure 5.3a. Around time zero we observe signs of the CA followed by GSB (~ 570 nm) and a SE band (>750 nm). Both signatures decay with the characteristic excited state lifetime of ~ 0.5 ps¹¹⁸ concomitant with the growth of the photoproduct absorption band around 640 nm. Signatures of VC are apparent in the form of oscillatory modulations of the electronic signal.

The isolated VC obtained after truncating the differential absorbance map at $t = 150$ fs and removing the electronic kinetics by fitting to a sum of two exponentially decaying functions ($\tau_0 = 520 \pm 50$ fs, $\tau_1 = 2.6 \pm 1$ ps) is shown in Figure 5.3b. Two phase jumps are present, one at 580 nm, slightly red shifted with respect to the ground state absorption spectrum and a second one at the border between ground and excited state signatures at 750 nm. The NIR VC is strongly damped compared to the one in the visible spectral range, in agreement with the short lifetime of the excited electronic state of ~ 500 fs. These observations suggest that the NIR VC might be dominated by S_1 and the visible VC by S_0 contributions.

Fourier transformation and averaging over the 520-720 nm and 775-880 nm wavelength regions reveals the frequency content of the VC as representative Fourier intensity spectra of the two regions (Figure 5.4). A comparison with the pre-resonance Raman spectrum recorded at 785 nm allows us to identify

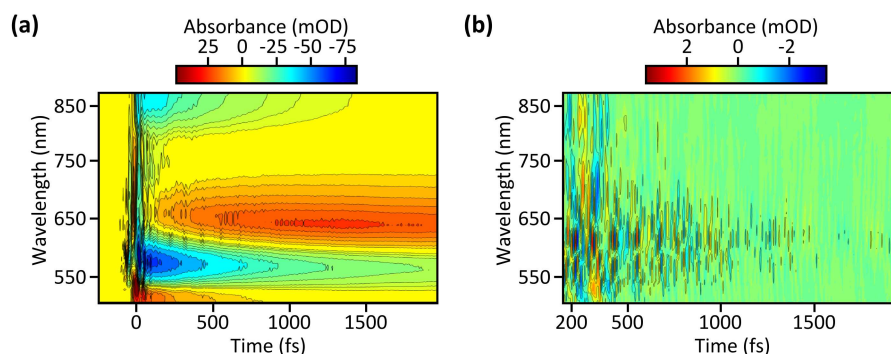


Figure 5.3: **Transient electronic kinetics and VC of bacteriorhodopsin (bR).** (a) Differential absorbance map recorded for bR following excitation with a 9.6 fs pulse. Pump and probe beams are focused to 100 and 60 μm diameter (at FWHM), with pulse energies adjusted to 200 and 2.5 nJ, respectively. (b) Residual VC isolated from (a) by exponential fitting. The black contour lines are a guide to the eye and were set to ± 1 mOD and ± 400 μOD

VC contributions from either the ground or excited electronic state. Throughout the spectral range, we find excellent agreement between the VC frequencies observed in the visible spectral region and the ground state Raman spectrum, even for smaller amplitude modes ($1100\text{-}1500\text{ cm}^{-1}$). This finding strongly suggests that we are observing VC activity on S_0 . The slight amplitude differences can be explained by the limited temporal resolution of our experiment. In the NIR spectral region we observe a drastically altered frequency and intensity distribution. Strong VC activity in the torsional, low frequency, region as well as several new bands $<1000\text{ cm}^{-1}$ is present. Additionally, the previously dominant ground state bands at 1168 , 1201 and 1526 cm^{-1} are almost absent from the spectrum. We thus assign most of the frequencies in the SE region to originating from S_1 . Some modes, however, exhibit line widths suggestive of lifetimes exceeding that of the S_1 state such as the sharp band around 1007 cm^{-1} . In short, some residual S_0 VC seems to be present in the spectral region of the SE transition hence rendering a clear assignment of the VC activity difficult.

Electronic population control of bacteriorhodopsin

We developed an experimental procedure based on electronic population control^{166,167} as outlined in Figure 5.5a to extract pure excited state VC activity (see Chapter 6 for more details). Photoexcitation of bR generates an ensemble

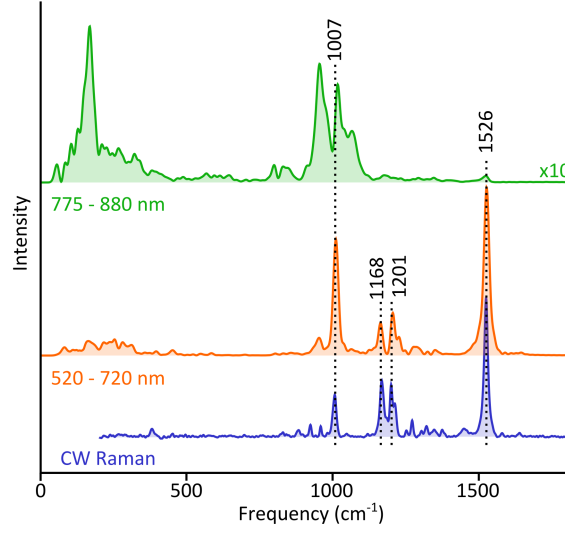


Figure 5.4: VC activity obtained for RPSB in bR in the SE (top) and GSB (middle) spectral regions compared to a ground state pre-resonance Raman spectrum. The black dotted lines indicate the most prominent ground state frequencies.

mixture of molecules in the ground or excited electronic state. In the case of an ultrashort pulse in resonance with the $S_1 \leftarrow S_0$ transition, VC on both states can be generated. A temporally long "dump" pulse, exclusively resonant with electronic transitions from the excited electronic state, depletes S_1 population, and with it VC as:

$$VC_{OFF} = \chi_{S_1} + \chi_{S_0}, \quad (5.1a)$$

$$VC_{ON} = (1 - x) \cdot \chi_{S_1} + \chi_{S_0}, \quad (5.1b)$$

$$VC_{OmO} = VC_{OFF} - VC_{ON} = x \cdot \chi_{S_1}, \quad (5.1c)$$

with VC_{OFF} and VC_{ON} being the VC recorded in the absence (dump_{OFF}) and presence (dump_{ON}) of the dump pulse and χ_i the VC on the electronic state i . By using a long enough dump pulse we exclude VC generation by population control and VC_{OmO} ($>100 \text{ cm}^{-1}$) should isolate the S_1 VC activity.

Experimentally, we use a 1 ps dump pulse centered at 880 nm (200 cm^{-1} bandwidth) time coincident with the pump pulse (Figure 5.5b). By employing a double chopping scheme, we record differential absorbance in the presence and absence of population control. As the dump pulse is solely resonant with electronic transitions from the excited state no measurable effect is detected

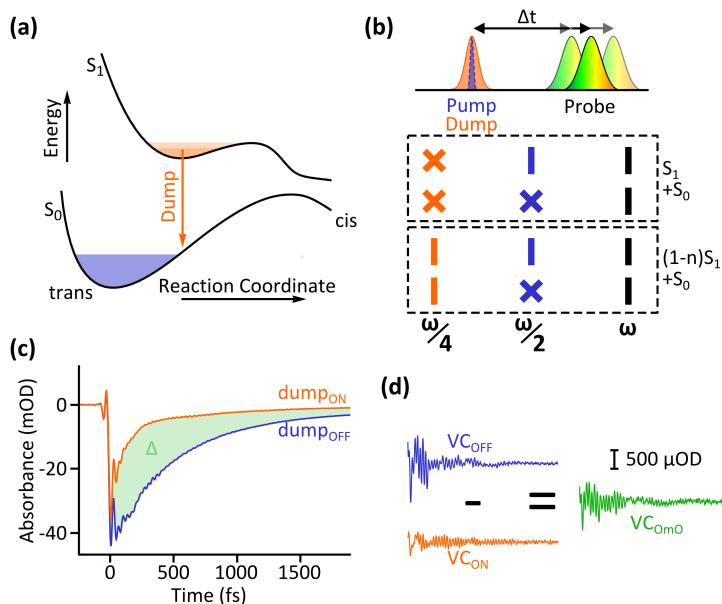


Figure 5.5: **Electronic population control for the isolation of excited state vibrational coherence.** (a) Concept of electronic population control for the isolation of excited electronic state VC. (b) Pulses and chopping scheme. Crosses indicate blocked and lines unblocked beams. (c) Differential absorbance recorded at 850 nm for bR in the presence (orange) and absence (blue) of the dump pulse. (d) Subtraction of the VC recorded at 850 nm in the absence (VC_{OFF}) and presence (VC_{ON}) of the dump pulse isolates VC present on, or originating from, S_1 (VC_{omO}).

prior to photoexcitation of the sample. Following population transfer from the ground to the excited electronic state, by the pump pulse, the dump depletes a fraction of the S_1 population via the SE transition thus resulting in an altered transient evolution (Figure 5.5c). The difference between the two residual VC, obtained after exponential fitting, should thus reveal pure S_1 contributions (Figure 5.5d).

Figure 5.6a shows the differential absorbance maps obtained in the presence and absence of the dump pulse as well as the difference between the two. As an effect of population control we observe a shorter excited state lifetime in combination with a reduction in photoproduct signal, in agreement with previous experimental observations.¹⁶⁵ The difference between $dump_{OFF}$ and $dump_{ON}$ appears similar to the electronic kinetics recorded in the absence of the dump pulse. The pronounced CA has, however, been eliminated from the differential map and the initial temporal evolution is convolved with the temporal envelope of the dump pulse.

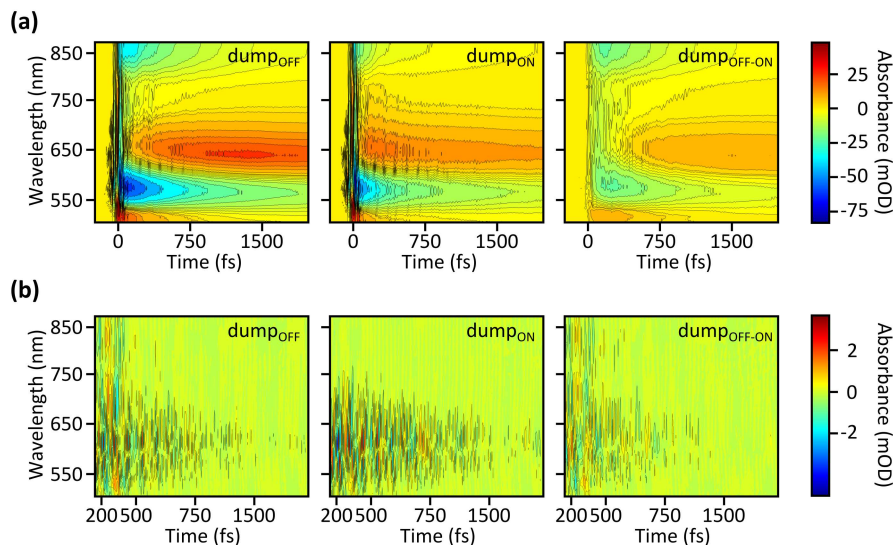


Figure 5.6: **Electronic population control of bacteriorhodopsin.** (a) Differential absorbance maps recorded for bR following excitation with a 9.6 fs pulse in the absence (left) and presence (middle) of the dump pulse as well as the difference between the two measurements (right). (b) Residual VC isolated from (a) after temporal truncating and exponential fitting.

Subtraction of the electronic kinetics reveals the underlying VC (Figure 5.6b). The short lived VC in the SE spectral region is removed efficiently, suggesting that its electronic origin is on S_1 . We, however, observe an increase in long lived VC amplitude in the visible spectral region of the dump_{ON} map and the difference between dump_{OFF} and dump_{ON} reveals residual oscillations with lifetimes exceeding those of S_1 .

To rationalise these findings we compare the Fourier intensity maps of the VC without and with population control (Figure 5.7a). In the GSB region the spectral dependence of the major ground state bands is resolved. A different intensity distribution for each frequency, reminiscent of mode specific vibronic transitions, is present. The SE region shows predominantly lifetime broadened bands and an overall altered spectral appearance confirming our previous observations based on the averaged spectra. The action of the dump pulse removes most of the broad features in the SE region but seems to enhance the band intensities around 1000 and 1520 cm^{-1} . In the GSB region we note a strong increase in Raman activity following SE depletion by the dump pulse.

We summarise these observations by generating representative average spectra in the 520-720 and 775-880 nm spectral range. Upon depletion of S_1 all

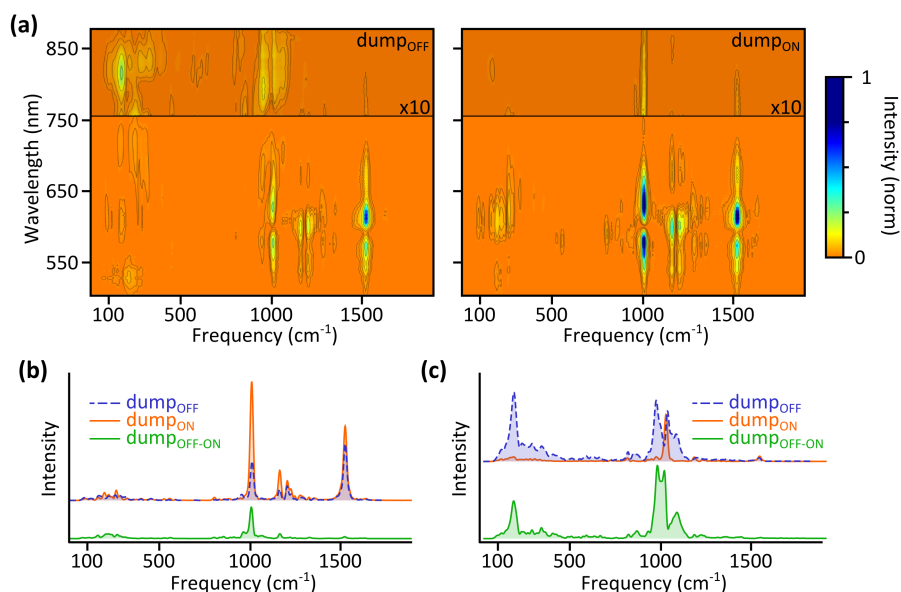


Figure 5.7: **Results of electronic population control of bacteriorhodopsin.**

(a) Fourier intensity map obtained from the dump_{OFF} VC (left) in comparison to dump_{ON} intensity (right). (b) Dump_{OFF}, dump_{ON} and dump_{OFF-ON} spectra obtained by averaging the 520-720 nm spectral region. (c) As (b) but for the 775-880 nm spectral region. We note that the magnitude of the visible difference between dump_{OFF} and dump_{ON} in comparison to dump_{OFF-ON} might seem incorrect. This difference is, however, merely a result of the spectra being intensity, rather than amplitude spectra.

known ground state bands in the visible spectral range increase in intensity and the difference reveals that the 1007 cm⁻¹ mode is especially affected (Figure 5.7b). All of these bands exhibit lifetimes exceeding the lifetime of S₁ and are hence not VC on the excited electronic state. In the SE region, however, satisfactory removal of short lived modes is achieved by population control. The difference between dump_{OFF} and dump_{ON} indicates that some long lived VC, as for example around 1000 cm⁻¹, might be contaminating the S₁ VC (Figure 5.7c).

To exclude the possibility of VC transfer by the dump pulse we perform control experiments on β -carotene and nBu-RPSB. In brief, we generate VC in the S₀ state, using a fully off-resonant impulsive pulses (10 fs) and then transfer most of the molecules into the excited electronic state with a 200 fs long actinic pump. We do not observe the emergence of any new VC signatures and thus conclude that VC transfer by means of an electric field induced population transfer is most likely not the origin of the S₁ VC contamination observed in

bR.

A second pathway for VC transfer could be the PES itself. We recently showed that internal conversion (IC) through conical intersections (CI)^{168–171} is vibrationally coherent.¹⁶⁷ Partial depletion of the S_1 state reduces the amount of VC that can transfer back onto the ground state. In the differential measurement, dump_{OFF-ON} , the indirectly depleted ground state VC will hence contribute to the S_1 spectrum. If the S_0 VC generated via IC from S_1 is out of phase with the impulsively generated ground state VC then a reduction in the former will result in an increase in the VC amplitude in the dump_{ON} experiment. The observation of this effect strongly suggests that the spectral leakage in bR must be caused by vibrationally coherent IC, from S_1 , through a CI. Additionally, not all ground state bands are affected in the same way, thus further pointing towards a PES mediated VC mechanism.¹⁷²

The spectral signatures in the visible suggest dominant contributions from bR with the RPSB chromophore in the all-*trans* configuration. A possibility could be the presence of an ultrafast channel (~ 100 fs) allowing for rapid IC of the non-isomerising molecules which would, furthermore, explain the identical isomerisation yields observed for rhodopsin and bR, despite the nominally five times slower reaction rate.^{116,118,156,173}

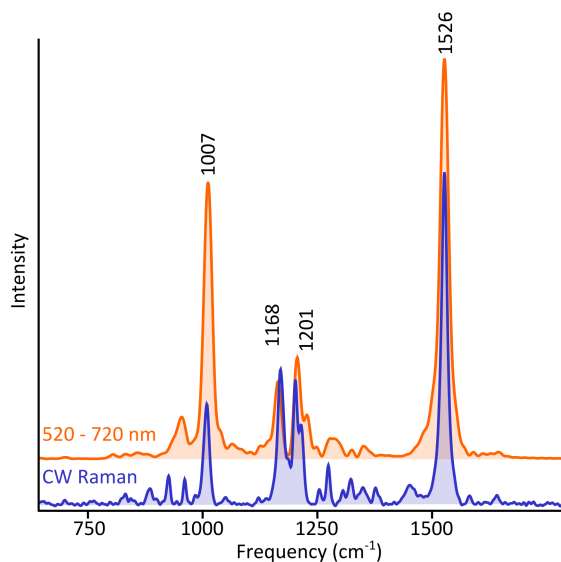


Figure 5.8: The spontaneous Raman spectrum of bR (blue) agrees well with the spectrum obtained from the VC of dump_{OFF} by averaging the visible spectral region (orange).

The presence of VC in all-*trans* ground state molecules suggests that it should be possible to, additionally, detect vibrational signatures of the photoproduct. Previous studies on both the J- and the K-intermediate have identified a 10 cm^{-1} red shift of the C=C stretching mode to $\sim 1517\text{ cm}^{-1}$ as well as an intense marker band at 1189 cm^{-1} as the predominant spectral signatures of the photoproduct.^{174,175} A comparison of the spontaneous Raman spectrum obtained for bR with the VC activity in the visible spectral region does, however, not allow for the conclusive identification of photoproduct VC (Figure 5.8). Minor differences between the spectra are nevertheless apparent, especially in the $1250\text{--}1400\text{ cm}^{-1}$ region, but the spectral complexity as well as the absence of a high-quality J-intermediate Raman spectrum renders a precise analysis difficult.

Isolating the pure excited state vibrational coherence of bacteriorhodopsin

To, nevertheless, isolate pure VC activity on S_1 we employ a fitting routine in combination with VC lifetime filtering. If we assume realistic vibrational dephasing times of $200\text{--}1500\text{ fs}$ and an excited state lifetime of 520 fs for bR, then the decay constants for S_1 VC should be in the $200\text{--}380 \pm 30\text{ fs}$ regime. VC with significantly longer lifetimes is most likely originating from the ground electronic state.

We average the VC in the $760\text{--}840\text{ nm}$ spectral region to increase the experimental sensitivity. To obtain a robust starting guess for both decay times and frequencies we use LPSVD.^{106,107} These initial parameters are fed into a fitting routine implemented in Labview that non linearly optimises both the exponential decay constants and frequencies using an LMA while linearly optimising oscillation amplitude and phase by Lower Upper (LU) decomposition. Although LPSVD reproduces the experimental VC remarkably well, the fitting routine improves the residual by another $10\text{--}30\%$ and additionally allows us to exclude non physical results such as exponentially increasing VC. A total of 24 oscillations are sufficient to describe both the experimentally obtained VC as well as the Fourier intensity spectrum (Figure 5.9). Increasing the number of variable parameters does not lead to an improvement in fit performance. We avoided any determination of vibrational phases due to the difficulties associated with precisely determining time zero in this experiment and the often non-trivial dependence of phase on detection wavelength.¹¹²

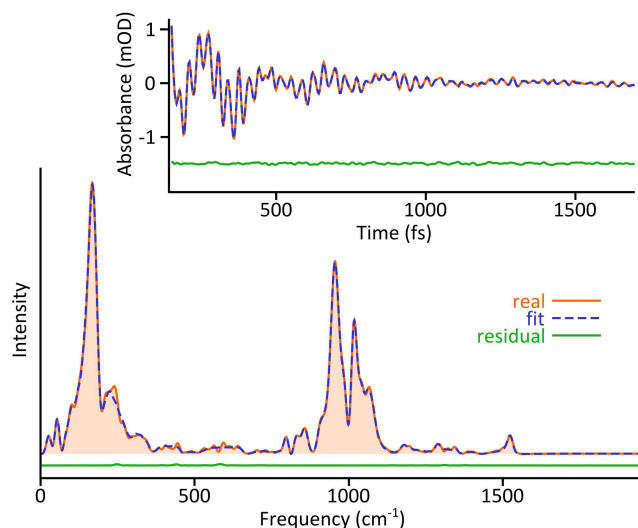


Figure 5.9: Fitting results and residuals obtained for a VC averaged in the 760-840 nm spectral region shown for both the frequency, as well as the time domain (inset).

The fitting results are summarised in Table 5.1. All frequencies outside of the $200\text{-}380 \pm 30$ fs range, apart from the known ground state bands at 1007 and 1526 cm^{-1} , exhibit small amplitudes $<200\text{ }\mu\text{OD}$ and hence a negligible contribution to the overall VC or spectrum.

The vibrational coherence activity of the excited electronic state of bacteriorhodopsin

After removal of the S_0 signatures we are left with a spectrum representative of VC activity on S_1 . To obtain a realistic estimate of the VC activity in the SE region we correct the Fourier intensities for our limited temporal resolution (see Chapter 3 for details). The resulting Fourier intensity spectrum of the S_1 VC activity exhibits a completely different intensity and frequency distribution compared to the ground state pre-resonance Raman spectrum (5.10). Hydrogen-out-of-plane wagging (HOOP) at 952 cm^{-1} dominates the spectrum, with lesser contributions from additional HOOP modes (900 cm^{-1}), Schiff base (1075 cm^{-1}), and backbone torsional (177 and 192 cm^{-1}) coordinates. Additionally, we observe some methyl-rocking activity (1005 cm^{-1}) as well as a band at 1425 cm^{-1} which might be due to methyl-deformation. Recent coherent infrared emission spectra on bR agree with our observation of strong activity

Frequency (cm ⁻¹)	Lifetime (fs)	Amplitude (μOD)
<i>20</i>	<i>1380</i>	<i>53</i>
<i>58</i>	<i>1409</i>	<i>54</i>
<i>91</i>	<i>256</i>	<i>375</i>
177	224	3818
192	161	5446
293	264	131
363	252	207
458	466	50
523	142	371
660	270	167
733	136	293
799	966	65
828	647	115
860	564	185
900	400	297
952	321	865
1005	173	1510
1007	535	280
1075	246	429
1171	332	103
1286	556	45
1355	824	24
1425	249	165
1526	530	122

Table 5.1: Fitting results obtained for the dump_{OFF} VC in the 760-840 nm spectral region. Frequencies indicated in bold are assigned to the ground electronic state, frequencies in italic are omitted due to their low frequency nature and hence possible interference with the exponential fit applied to remove the electronic kinetics.

in the 750-1150 cm⁻¹ region, but an unambiguous assignment of the observed features was hampered by numerous additional modes of unknown origin.¹⁷⁶

An important consequence of our detection methodology is that vibrational motion which strongly modifies the S₀-S₁ energy gap necessarily generates the most prominent oscillatory features in the transient electronic spectra (Figure 5.2b). Given that the critical step during the isomerisation reaction is the passage from S₁ to S₀ through a CI, the most active modes in our experiment are likely to be the strongest contributors to excited state decay and thus the photoisomerisation. Despite the complexity of the system with more than 300 nuclear degrees of freedom, the S₁ VC of RPSB in bR is dominated by a HOOP mode at 952 cm⁻¹, a motion essential to C=C isomerisations²⁹ and capable of

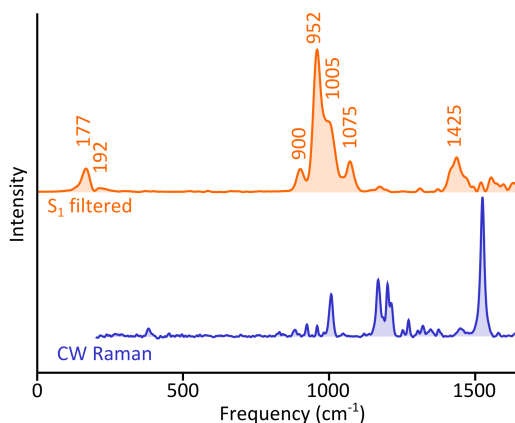


Figure 5.10: Pure vibrational coherence activity obtained for the S_1 electronic state of bR after correction for temporal resolution (orange) in comparison to the S_0 pre-resonant Raman spectrum (blue).

coupling the ground and excited electronic states PES. The results presented in Figure 5.10 thus suggest a correspondence between the ability of a system to focus energy into a few critical coordinates and the photochemical outcome of excited state decay.

Vibrational dephasing times on the time scale of, or longer than, the excited state lifetime are necessary to markedly influence the reactivity of a system. If the electronic surface crossing takes too long then the initially focused vibrational activity thermalises and potentially beneficial effects are lost. We compute the vibrational dephasing times to being ~ 900 fs for the HOOP mode at 952 cm^{-1} and ~ 400 fs and ~ 520 fs for the torsional degrees of freedom at 177 and 192 cm^{-1} , respectively. These time scales are sufficiently long compared to the 520 fs excited state lifetime of bR to markedly influence the photochemical outcome of the photoreaction. We rationalise the surprisingly fast vibrational dephasing times of the torsional modes as being caused by decreasing Raman cross sections as the system approaches the CI region, most likely due to anharmonicity induced dephasing.

An unreactive comparison

Although such an interpretation is appealing, it does not prove a correlation between the observed VC activity, the shape of the PES and photochemical reactivity. We ^b therefore synthesis an RPSB chromophore with p-methoxyaniline

^bSynthesis and characterisation of pma-RPSB was performed by Giovanni Bassolino

(pma) as the base to completely eliminate all isomerising channels.¹⁵⁹ The structure of pma-RPSB is shown in Figure 5.11.

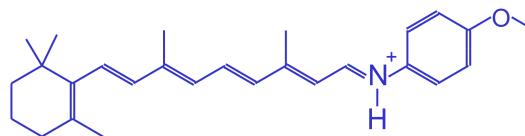


Figure 5.11: Molecular structure of pma-RPSB.

We perform geometry optimisations and frequency calculations using B97XD/cc-pVDZ as implemented in Gaussian09^{177,178} for both pma-RPSB as well as nBu-RPSB as a calculation benchmark¹⁷⁹ to assign the major Raman frequencies of pma-RPSB^c. Solvent effects are considered via the CPCM model (methanol for nBu-RPSB and acetonitrile for pma-RPSB).¹⁸⁰ The vibrational frequencies obtained are scaled by a factor of 0.978 to match the major C=C stretching mode of the experimentally obtained pre-resonance Raman spectra. After convolution of the calculated Raman activities with a Lorentzian function with a FWHM of 4 cm⁻¹ we obtain the Raman spectra shown in Figure 5.12.

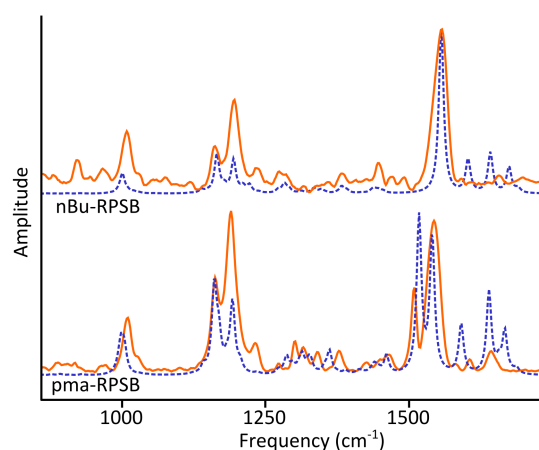


Figure 5.12: Experimental (solid, orange) and theoretical (dashed, blue) Raman spectra for nBu-RPSB (top) and pma-RPSB (bottom).

The close resemblance of the S_0 Raman spectrum of pma-RPSB to that of nBu-RPSB and hence RPSB in bR (compare Figure 5.1b) suggests similar ground state geometries, excited electronic state character, and initial nuclear

^cThe calculations were performed by Christoph Schnedermann

evolution for RPSB in bR and pma-RPSB in solution.^{113,181} Additionally, we are able to assign the major frequencies to the same normal modes with the apparent differences being caused by coupling to the pma Schiff base moiety. As a result we are able to attribute any differences in the VC activities of bR and pma-RPSB to the specific excited state potential rather than to differences in the initial ground state configuration or electronic state character of the S_1 state.

We perform a TA experiment similar to the one on bR but with a 6.8 fs pulse in resonance with the $S_1 \leftarrow S_0$ transition of pma-RPSB (Figure 5.13a) to extract its VC activity. The differential absorbance map (Figure 5.13b) exhibits a CA around time zero rapidly followed by GSB and SE signatures centered at 560 and 810 nm, respectively. In contrast to bR, the photoinduced absorption band around 650 nm is not a signature of photoproduct formation but instead an ESA band of S_1 ¹⁵⁹ that decays with the same time constant as the SE. To isolate the VC, we truncate the differential absorbance map at $t = 150$ fs and remove the electronic kinetics by exponential fitting.

A representation spectrum of the S_1 VC activity averaged over the SE region (760-850 nm), in comparison to the ground state pre-resonance Raman spectrum, is presented in Figure 5.13c. None of the bands observed in the excited state spectrum resembles ground state frequencies and we hence did not apply the fitting procedure to remove possible S_0 contributions. In contrast to RPSB in bR the S_1 VC shows negligible activity in the HOOP (<1000 cm^{-1}) and torsional (<300 cm^{-1}) regions of the spectrum and is instead dominated by stretching coordinates with significant contributions likely originating from the aromatic Schiff base moiety (1000-1300 cm^{-1}), as suggested by the changes observed in the VC intensity when repeating the experiment on pma-RPSB with a fully deuterated pma base (Figure 5.13c).

5.3 Discussion

In contrast to most current ultrafast techniques, the VC studied here is generated by the photon that triggers the light-induced process. Our results thus do not simply report on the structural evolution of the molecule of interest, but instead on the coherent vibrational energy flow along the S_1 PES out of the FC region during the photoisomerisation reaction. Based on the S_0 Raman spectra, we would have expected strong VC activity in backbone stretches for

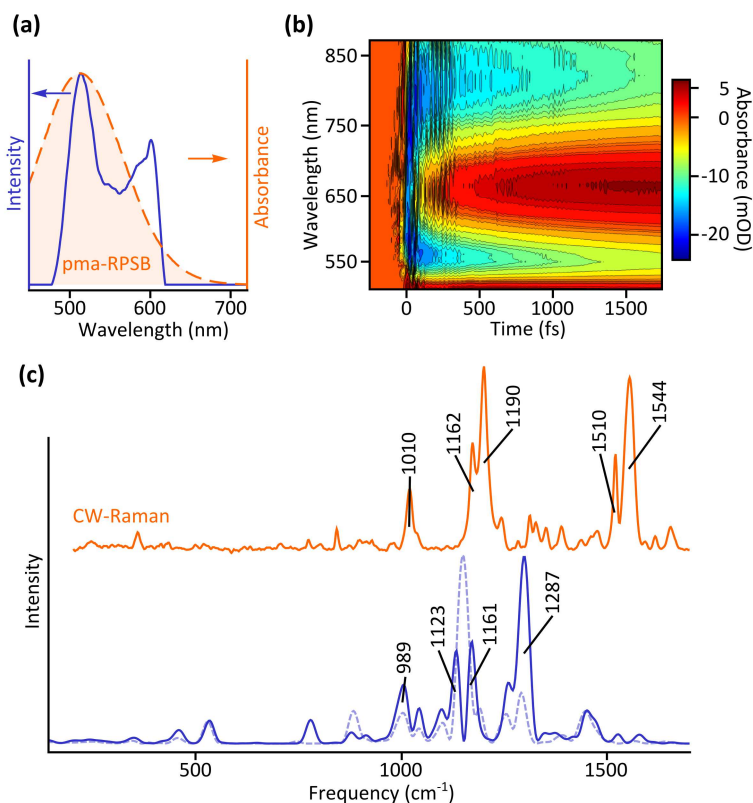


Figure 5.13: **Extracting vibrational coherence activity of pma-RPSB.** (a) 6.8 fs excitation pulse (solid, blue) and absorption spectrum of pma-RPSB dissolved in methanol (orange, dashed). (b) Differential absorbance map recorded for pma-RPSB dissolved in methanol ($OD_{max} = 1$ in the 200 μm flow cell used during the experiment). Pump and probe beams are focused to 65 and 46 μm diameter (at FWHM), with pulse energies adjusted to 20 and 2.5 nJ, respectively. (c) VC intensity of pma-RPSB (blue, solid) and fully deuterated pma-RPSB (blue, dashed) averaged over the 760–850 nm spectral region in comparison to a S_0 pre-resonance Raman spectrum recorded at 785 nm.

both RPSB in bR and in pma-RPSB, but observed exactly the opposite experimentally (compare Figure 5.10 and 5.13c). In fact, given that S_1 VC is generated mainly in FC active modes, we would expect the Fourier intensity spectra of the S_1 VC activity for pma-RPSB and RPSB in bR to be as similar as the respective ground electronic state Raman spectra.

The huge discrepancy between the S_0 Raman spectrum and the VC activity cannot be solely attributed to vibrational structural changes caused by different bonding properties upon electronic excitation. The apparent lack of backbone stretching activity in bR is *a priori* surprising, given the dominant presence

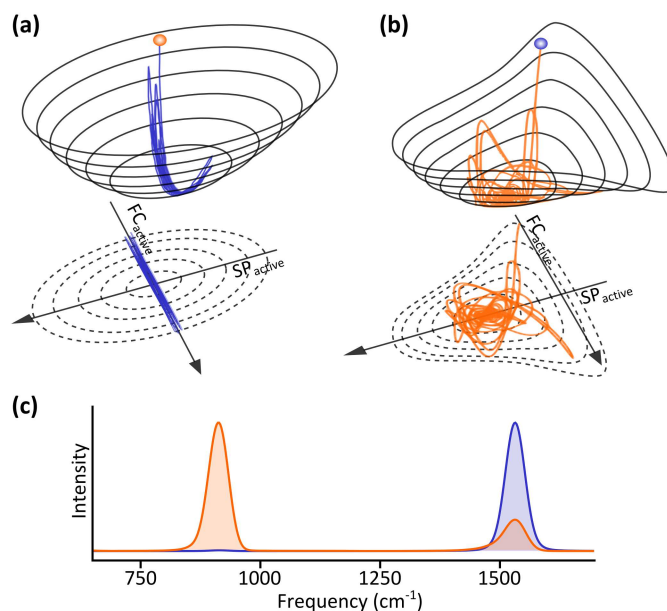


Figure 5.14: **Anharmonic coupling as a mediator for efficient photoisomerisation.** (a) PES and classical trajectory for two uncoupled nuclear coordinates, with only one coordinate being significantly displaced with respect to the ground electronic state. (b) PES and dynamic evolution for identical initial displacements as in (a), but with the addition of an anharmonic coupling term. (c) Fourier intensity obtained for the wavepacket trajectory of the harmonic (orange) and anharmonic (blue) PES.

of C=C stretching modes in the Raman spectra of polyenic systems. Such behavior, however, has been previously observed in the photoisomerisation of *cis*-stilbene.¹⁸² The key question thus relates to the mechanism by which VC can appear in initially silent and disappear from initially excited degrees of freedom. The latter can be explained by a change in equilibrium displacement between S_0 and S_1 as the structure of the molecule evolves on the excited electronic state. The former, however, must be related to the shape of the PES away from the FC region.¹²⁹

To demonstrate possible effects of the PES on the VC activity we simulate a two-dimensional excited state PES consisting of two uncoupled nuclear coordinates, only one of which is displaced from its equilibrium position in the FC region^d. For a $\pi^* \leftarrow \pi$ transition, two such coordinates could be the symmetric C=C stretch and an asymmetric HOOP. Upon population of the S_1 electronic state, the system oscillates along the displaced stretching coordinate around its

^dThe classical wavepacket trajectories were calculated by Christoph Schnedermann.

new equilibrium bond length but without gaining any momentum along the initially silent asymmetric HOOP (Figure 5.14a). By introducing a coupling term between the two modes we are able to drastically change this behavior. The system now gains momentum along the asymmetric coordinate after the first tens of femtoseconds, even if the initial displacement was close to zero (Figure 5.14b). Such a shift, however, does not necessarily induce significant changes in the resonance Raman spectra, as only the earliest dynamics are sampled.¹⁵² For both PES the system originally oscillates around the C=C stretching coordinate. Computing the Fourier transformation of the VC activity, however, shows that the initially silent asymmetric HOOP mode is efficiently activated by anharmonicity induced VC transfer (Figure 5.14c).

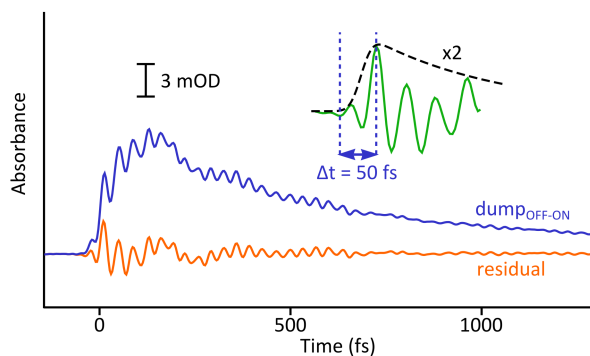


Figure 5.15: Recording the differential absorption in the 760-840 nm spectral region in the presence and absence of a dump pulse in resonance only with the $S_0 \leftarrow S_1$ transition removes the CA (Figure 5.5c) around time zero and reveals the rapid rise of the coherent vibrational activity. Inset: magnification of the rising coherence amplitude.

To quantify the time scale for the coherent vibrational coupling process,¹⁸³ we use population control to eliminate the otherwise dominant CA around time zero, thus revealing the full temporal evolution of the VC down to the earliest time delays (see Figure 5.6a). We observe a rapid rise of the VC on the <50 fs time scale (Figure 5.15). Interestingly, this growth is comparable to the recently reported rise time of the SE signal and matches the kinetics of tentatively assigned excited state signatures at wavelengths $>1 \mu\text{m}$.^{153,164} The major changes responsible for the observed VC transfer therefore likely take place during the first tens of femtoseconds after photoexcitation.

5.4 Conclusion and Outlook

In conclusion, we used ultrabroadband TA spectroscopy with high temporal resolution to reveal the coherent nuclear response of a molecule after absorption of a photon. We, for the first time, recorded and assigned VC on an excited electronic state over the full vibrational manifold (100-2000 cm^{-1}). In contrast to the expectation that the photon-induced structural evolution largely takes place along FC active coordinates, we observed efficient and coherent activation of initially silent vibrational modes most likely caused by PES-induced anharmonic coupling. We furthermore demonstrated that the nature of the coherent evolution differs dramatically with the environment of the molecule and is strongly correlated with the efficiency and outcome of the light induced process as evidenced by the comparison of RPSB in bR and pma-RPSB in solution. The protein likely achieves high efficiency and specificity by shaping the PES with charged residues in the binding pocket,^{184,185} a mechanism that is unavailable in solution where a completely different photoproduct is formed.

Interestingly, the coherent evolution takes place on the <50 fs time scale, fast enough to allow for quantum coherent effects to remain active and decisive for the eventual outcome of the process. This mechanism holds even for natural light excitation with <5 fs coherence times since the decisive factor is the homogeneous line width of the excited transition.¹⁸⁶

Chapter 6

Vibrationally coherent intersystem crossing of β -carotene

Parts of this chapter have been adapted from the following publication: Liebel, M., Schnedermann, C., Kukura, P., *Phys. Rev. Lett.* **2014**, 112, 198302¹⁶⁷ and are copyright (2014) by the American Physical Society. All work presented in this chapter was performed by myself.

6.1 Introduction

Conical intersections (CI) between potential energy surfaces (PES) are a dominant concept in the theoretical description of ultrafast electronic surface crossings in polyatomic molecules.^{168–172} According to this theoretical treatment a subset of vibrational degrees of freedom mediates the efficient coupling of electronic states. Experimentally, it is, however, difficult to identify such coordinates.^{187–189} VC should be an ideal tool to study CI dynamics, because the nuclear wavepacket evolution has been predicted to be strongly dependent on how a respective vibrational coordinate is involved in the surface coupling.^{172,190}

Previous experimental studies on polyatomics succeeded in probing VC after electronic surface crossing^{16,22} but only in low frequency ($<200\text{ cm}^{-1}$) modes with associated vibrational periods on the order of, or shorter than, the electronic surface crossing time. As a result it has not been possible to distinguish VC generated by the surface crossing from those surviving passage through the CI.

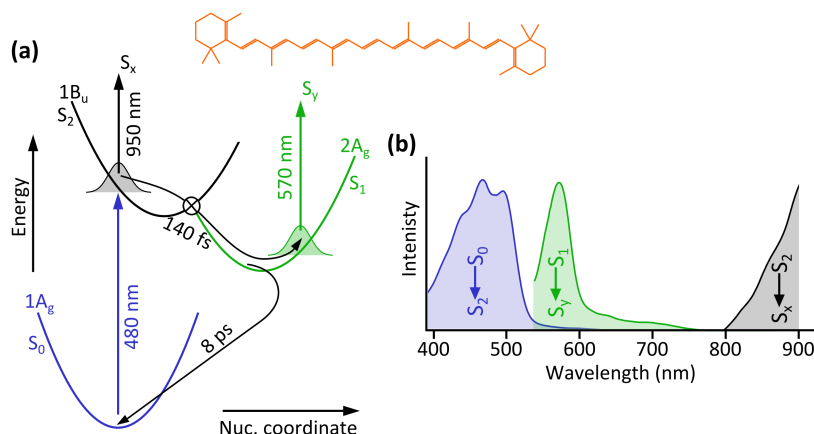


Figure 6.1: **Photophysics of β -carotene.** (a) Schematic of the potential energy scheme of β -carotene dissolved in toluene. (b) One-photon absorption spectra of the three energetically lowest singlet electronic states.

To experimentally address the question of how VC is affected by CI mediated surface crossings we employ β -carotene as a benchmark system.¹³⁰ One photon excitation with a short, ~ 10 fs, pump populates the second excited singlet state (S_2) which rapidly internally converts, within ~ 140 fs, into S_1 via a CI (Figure 6.1a). Direct, one photon, $S_1 \leftarrow S_0$ excitation is forbidden by symmetry. The possibility to selectively generate VC in S_2 in combination with an IC time faster than common vibrational dephasing rates make this system an ideal candidate for a proof of principle experiment. Additionally, the spectrally well separated S_0 , S_1 and S_2 absorption bands facilitate the assignment of VC to a respective electronic state of origin. We are able to monitor the S_2 ESA band and hence follow the initially generated VC. Due to the broad spectral range of our WL probe we can, simultaneously, observe the possible arrival of VC on the S_1 state (Figure 6.1b).

6.2 Experimental results

Pre-resonant excitation

The fate of VC upon IC through a CI in β -carotene has been previously studied by Cerullo *et al.*^{18,191} employing ~ 7 fs pulses in a degenerate pump and probe experiment. In their work the authors concluded that VC is lost upon $S_2 \rightarrow S_1$ internal conversion (IC), most likely due to the presence of a strongly anharmonic PES.

An alternative explanation for the absence of S_1 VC is the poor overlap of the $S_2 \leftarrow S_0$ absorption spectrum and the spectral extent of the excitation pulse (Figure 6.2a). Even though their nominal temporal resolution was excellent, the ability to superimpose multiple vibrational eigenstates and hence generate VC in high-frequency modes on the excited electronic state is highly diminished (Figure 6.2a inset). If no VC on S_2 can be generated then the lack of VC activity in S_1 , after IC, does not prove that the IC process itself is vibrationally incoherent.

An additional reason for the absence of VC has recently been provided by Cerullo *et al.* themselves.⁹⁴ They showed, both theoretically and experimentally, that the temporal-resolution in a TA experiment is determined by the so-called "preparation window", that is, the overlap between the excitation pulse spectrum and the absorption spectrum of the species of interest. Given the poor spectral overlap (Figure 6.2a), the temporal-resolution for excited state VC generation in β -carotene is likely ~ 30 fs or worse.⁹⁴ For ground state VC, however, the temporal-resolution remains high, as the VC generation efficiency for off-resonant impulsive Raman scattering is solely determined by the pulse bandwidth. As a result Cerullo *et al.* observed no S_1 VC even though high frequency ground state VC was present and concluded that the IC process from S_2 into S_1 must be vibrationally incoherent.

To address the question whether the absence of S_1 VC is due to vibrationally incoherent IC or solely a result of insufficient S_2 VC generation we repeat the experiment of Cerullo *et al.* but with the additional capability of probing both the S_2 and the S_1 ESA transitions. This experimental modification allows us to both monitor possible S_1 VC as well as to verify if S_2 VC is generated upon photoexcitation. An 11 fs pump pulse pre-resonant with β -carotene dissolved in deuterated chloroform excites the system into the second excited state (Figure 6.2b). By stepping the pump-probe delay we record a differential absorbance map of the systems evolution after photoexcitation. Following WL chirp correction and truncation of the map at $t = 80$ fs we remove the residual electronic kinetics by exponential fitting and isolate the VC. The VC activity in the $S_y \leftarrow S_1$ ESA region, in form of Fourier intensity spectra of the residual VC, is shown in Figure 6.2c.

All spectra are dominated by solvent bands with additional contributions from the well known ground state frequencies at 1008, 1162 and 1529 cm^{-1} . We note the complete absence of the up-shifted C=C stretching mode around

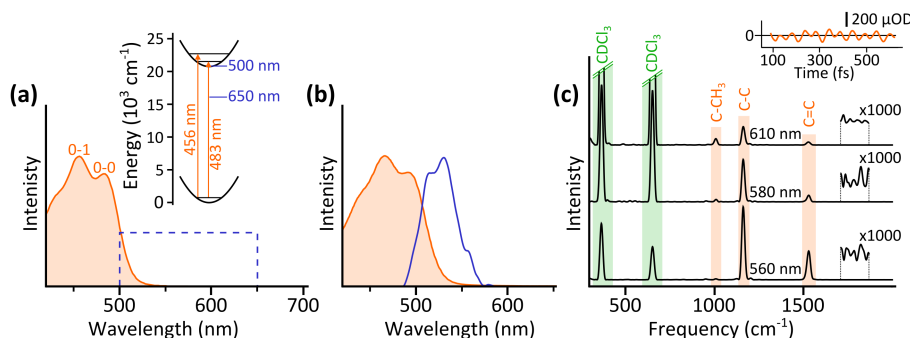


Figure 6.2: **Excited state vibrational coherence in β -carotene with pre-resonant excitation.** (a) Comparison of the $S_2 \leftarrow S_0$ absorption spectrum of β -carotene dissolved in cyclohexane (orange) with the spectral window of the excitation pulse used in previous experiments (blue, dashed).^{18,191} Inset: Energetic representation of the "0-0" and "0-1" transitions in β -carotene in comparison to the excitation energy available. (b) Comparison of the $S_2 \leftarrow S_0$ absorption spectrum of β -carotene dissolved in deuterated chloroform (orange) with the excitation pulse used in our experiment (blue). (c) Representative VC activity spectra in the $S_y \leftarrow S_1$ ESA region after photoexcitation of β -carotene. Inset: VC in the $S_x \leftarrow S_2$ absorption region at 850 nm shows no short lived contributions. The experimental parameters are: 60 nJ pump, $60 \times 110 \mu\text{m}$ focus (at FWHM); 2 nJ probe, $40 \times 80 \mu\text{m}$ focus (at FWHM); β -carotene at an $\text{OD}_{\text{max}} = 1$ in a $200 \mu\text{m}$ flow cell.

1800 cm^{-1} which serves as a background free marker for possible S_1 VC activity.¹³¹ To address the question whether the absence of S_1 VC activity is due to vibrationally incoherent IC we examine the residual VC in the S_2 ESA region (Figure 6.2c inset). For the short lived (~ 200 fs in deuterated chloroform) S_2 state we would expect rapidly decaying VC signatures. No such behavior is observed and the only contributing VC originates from solvent oscillations.

This finding has important implications: only a fully resonant excitation pulse will ensure sufficient spectral overlap to generate S_2 VC in β -carotene and it is hence necessary to blue shift the excitation pulse. The work by Cerullo *et al.* and our experiment agree in the experimental observation of no S_1 VC activity but by extending our probing bandwidth we are, however, able to demonstrate that the VC absence is not a proof of vibrationally incoherent IC from S_2 .

Resonant excitation

To monitor the coherent vibronic dynamics of β -carotene we perform a TA experiment with a 12 fs pump pulse, fully resonant with the $S_2 \leftarrow S_0$ transition

and simultaneously monitor the systems evolution in the S_2 and S_1 electronic states with a broadband WL probe (Figure 6.3).

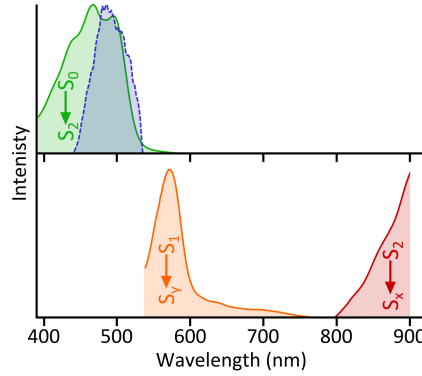


Figure 6.3: Absorption spectra of the ground (green), the first (orange) and second (red) excited electronic state of β -carotene dissolved in toluene as well as the spectrum of the 12 fs excitation pulse (blue, dashed).

We record the systems evolution as a function of pump-probe delay in the form of the wavelength resolved differential absorbance map shown in Figure 6.4a. The dominant CA at early time delays (<100 fs) is quickly followed by a weak bleach signal at wavelengths <530 nm, signs of SE in the 530-650 nm region,¹³⁸ and ESA from the S_2 state in the NIR >800 nm. The decay of the $S_x \leftarrow S_2$ and the rise of the $S_y \leftarrow S_1$ ESA features proceed with the same time constant of 140 fs, in agreement with previous results.¹³⁸

We truncate the differential absorbance map at $\Delta t = 85$ fs to avoid contamination by the CA. Globally fitting and subtracting the slowly varying electronic kinetics cleanly isolates the underlying VC (Figure 6.4b). Three major regions of VC activity are present. The NIR VC (>800 nm, S_2 ESA) decays rapidly with a time constant comparable to the S_2 lifetime, VC in the visible (540-650 nm, S_1 ESA) dephases more slowly and exhibits a phase jump around 570 nm,¹⁰¹ while weak and slowly decaying oscillations separate the two regions (650-800 nm). The spectral dependence (compare Figure 6.4a and b), as well as the phase jump suggest that the visible and NIR regions are dominated by S_1 and S_2 VC, respectively. The transition region (650-800 nm) highlights the fact that S_0 and solvent VC is impulsively generated and necessarily contributes over the entire observation window.

An averaged Fourier intensity spectrum of the 540-650 nm spectral range reveals the spectral content of the VC in the S_1 ESA region. Comparison to

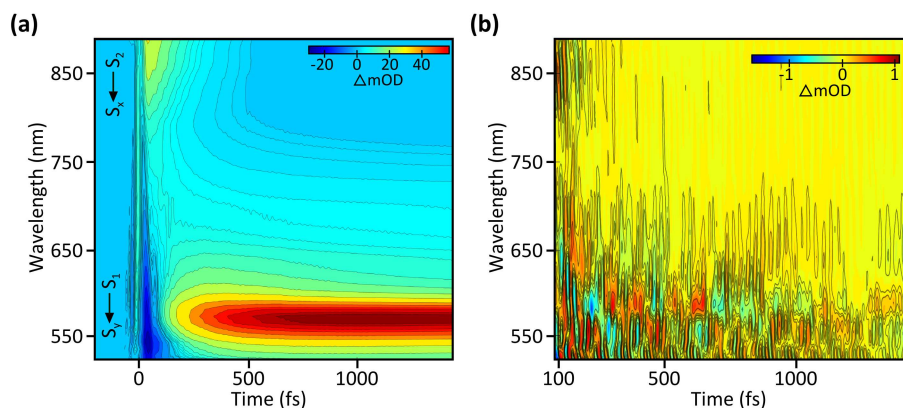


Figure 6.4: **Transient electronic kinetics and VC of β -carotene.** (a) Chirp corrected differential absorbance map of β -carotene dissolved in toluene ($OD = 0.7$ in a $200 \mu\text{m}$ flow cell) after photoexcitation with a 12 fs pulse centered at 480 nm. (b) Residual VC obtained from (a) after subtraction of the electronic kinetics. The experimental parameters are: 15 nJ pump, $75 \mu\text{m}^2$ focus (at FWHM); 1.5 nJ probe, $50 \mu\text{m}^2$ focus (at FWHM)

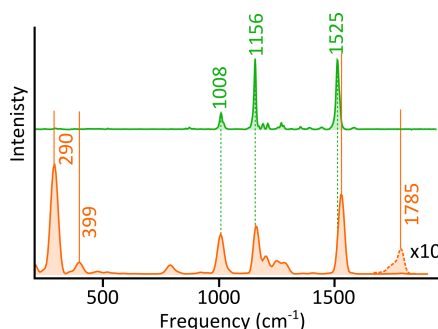


Figure 6.5: Comparison of a spontaneous Raman spectrum of β -carotene (green) to the Fourier intensity spectrum averaged over the 540-650 nm spectral region.

the ground electronic state spontaneous Raman spectrum reveals strong S_0 signatures at 1008 and 1156 cm^{-1} as well as clear S_1 features, such as the well-established 1785 cm^{-1} C=C stretching mode (Figure 6.5). Comparison to the S_1 spectrum obtained with BB-IVS on β -carotene dissolved in cyclohexane (compare Chapter 4) furthermore allows us to identify the bands at 290 and 399 cm^{-1} as originating from S_1 .^{51,115} Although these observations suggest that VC in multiple degrees of freedom is transferred from S_2 , through the CI, into S_1 , the presence of solvent and S_0 VC greatly diminishes the spectral quality and renders a detailed analysis of the S_1 -only contributions difficult.

Population control

As outlined in Chapter 5, electronic population control allows us to directly isolate VC of an electronic state of interest. In the case of bR we attempted to extract pure S_1 VC but failed, most likely due to the presence of a vibrationally coherent surface crossing pathway from S_1 into S_0 .¹⁴⁹

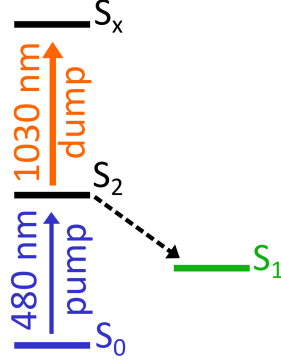


Figure 6.6: Electronic population control isolates excited state VC by depleting S_2 population with a 1 ps long dump pulse centered at 1030 nm, 150 nJ with a $85 \mu\text{m}^2$ focus (at FWHM).

By tuning the dump pulse into electronic resonance with the $S_x \leftarrow S_2$ ESA we selectively remove S_2 population and with it VC (Figure 6.6). Direct one-photon excitation from S_0 into S_1 is symmetry forbidden. As we are able to isolate S_1 VC by depleting S_2 we conclude that the former must be originating from the latter:

$$\text{VC}_{OFF} = \chi_{\beta car_{S_2, S_2 \rightarrow S_1}} + \chi_{\beta car_{S_0}} + \chi_{solvent}, \quad (6.1a)$$

$$\text{VC}_{ON} = (1 - x) \cdot \chi_{\beta car_{S_2, S_2 \rightarrow S_1}} + \chi_{\beta car_{S_0}} + \chi_{solvent}, \quad (6.1b)$$

$$\text{VC}_{OmO} = \text{VC}_{OFF} - \text{VC}_{ON} = x \cdot \chi_{\beta car_{S_2, S_2 \rightarrow S_1}}. \quad (6.1c)$$

With VC_{OmO} being the difference between the VC recorded in the presence (VC_{ON}) and absence (VC_{OFF}) of the dump pulse. x is the fraction of molecules removed from S_2 by the dump pulse and χ_j the VC of species j . VC_{OmO} therefore isolates VC that is either present on or originates from S_2 . Comparison of Figure 6.4b and 6.7a in the 650-800 nm spectral region highlights the efficient removal of all ground state and solvent VC. Two regions of pronounced VC activity remain: the $S_x \leftarrow S_2$ and the $S_y \leftarrow S_1$ ESA regions with wavelength

dependent VC amplitudes reminiscent of the respective transient absorption spectra (compare Figure 6.1b and 6.4a) and excited electronic state lifetimes.

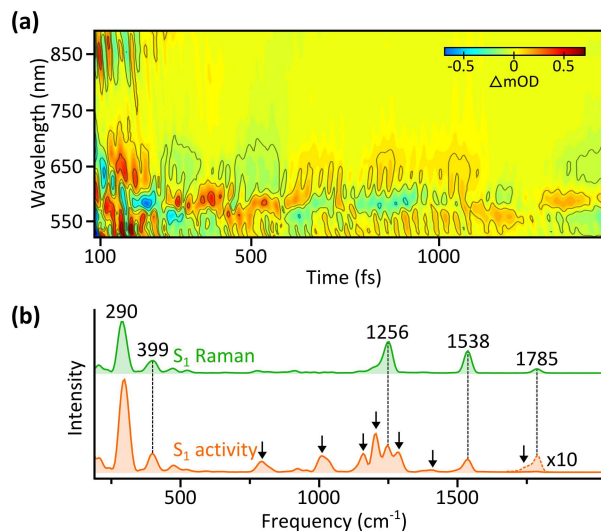


Figure 6.7: **Electronic population control isolates excited state VC.** (a) Excited state only VC map obtained as the difference between the VC recorded in the absence and presence of the dump pulse. (b) Comparison of a Fourier intensity spectrum obtained by BB-IVS (green) to the S_1 VC activity obtained by IC from S_2 (orange). Strongly enhanced bands are indicated by black arrows.

To capture a representative spectrum of the pure S_1 VC activity after IC from S_2 we generate a Fourier intensity spectrum of the 540-650 nm spectral region and compare it to a spectrum of the S_1 electronic state of β -carotene, dissolved in toluene, recorded via BB-IVS (Figure 6.7b). The major S_1 frequencies agree well over the entire spectral range but the intensities differ considerably. We observe comparable intensity ratios for the 290, 399, 1256 and 1538 cm^{-1} bands but numerous bands, marked with arrows, are strongly enhanced in the spectrum of VC_{OmO} when compared to the S_1 spectrum recorded via BB-IVS (Figure 6.7b). We note, that the enhanced bands are not newly emerging frequencies but are already present in the S_1 Raman spectrum albeit at almost negligible intensities.

The wavelength dependent VC activity is shown as a Fourier intensity map in Figure 6.8. In contrast to the visible spectral region, broad S_2 signatures dominate in the NIR. Even though the S_2 VC amplitude is considerable (Figure 6.7a), their contribution to the respective Fourier intensity map is almost negligible, a result of the rapid loss of electronic population caused by the short S_2

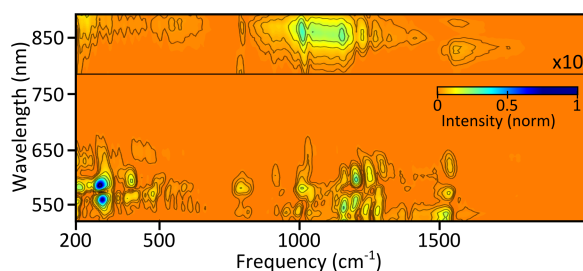


Figure 6.8: Fourier intensity map of the excited state only VC as a function of detection wavelength, the VC in the S_2 region has been magnified for clarity.

lifetime. Interestingly, we observe sharp features on top of the broad S_2 bands in the 780-880 nm region. Fourier intensity spectra necessarily merge phase and amplitude information (see Chapter 3), an effect that can influence both the band shape as well as the peak position, especially for partially overlapping bands.¹¹² These artefacts can become severe if narrow bands are superimposed onto broad features. To, nevertheless, obtain realistic frequency estimates and hence information on the vibrational dephasing times, we apply LPSVD to the VC observed in the visible (595-660 nm) and NIR (800-880 nm) spectral regions, results of which are shown in (Figure 6.9a).

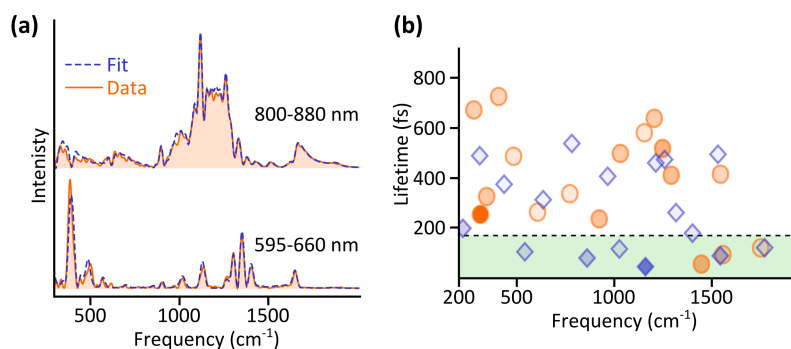


Figure 6.9: **Spectral content of the VC in the S_2 and S_1 spectral regions.** (a) Fourier intensity spectra (orange, solid) in comparison to results obtained by LPSVD (blue, dashed) in the S_2 (800-880 nm) and S_1 (595-660 nm) ESA regions. (b) Frequency content of the S_1 (circles) and S_2 (diamonds) regions. The symbol opacity represents the band amplitude.

Most of the VC activity in the S_2 region is concentrated in modes with fast (<140 fs) dephasing times, as expected for VC on a short lived electronic state such as S_2 . Some bands, however, as for example those present in the 1100-1400 cm^{-1} region, exhibit vibrational dephasing times that markedly exceed

the electronic lifetime of S_2 . These long-lived VC match those present in the S_1 spectral region, suggesting that several S_1 frequencies might be modulating the probe intensity in the spectral window of the S_2 ESA, even after the electronic state has nominally decayed.

6.3 Discussion

Our results clearly demonstrate that VC generated in one electronic state can be transferred to a different electronic state by IC through a CI. Despite $S_2 \leftarrow S_0$ optical excitation into the second excited state that decays with a 140 fs time constant into S_1 , VC in all known S_1 modes is present throughout the $S_2 \leftarrow S_1$ ESA window, even for vibrational periods as short as 19 fs (1785 cm^{-1}). Therefore, the origin of the observed S_1 VC must be at time zero, but in a different electronic state.

To understand the potential mechanism of the VC transfer, it is instructive to consider the role of nuclear degrees of freedom in electronic surface crossings. By definition, a CI is spanned by a subset of vibrational coordinates, known as coupling modes¹⁹⁰ while others, being important for reaching the CI, are classified as tuning coordinates.¹⁹² According to this theoretical framework, nuclear wavepackets in coupling modes can be strongly influenced by passage through the CI while VC in tuning modes remains largely unaffected by the surface crossing.

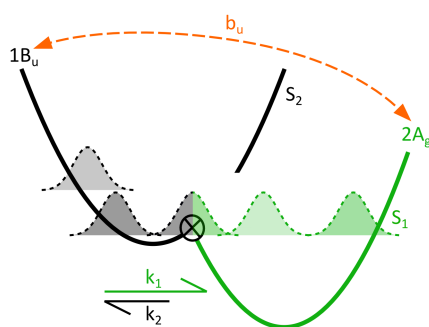


Figure 6.10: Vibronic coupling mechanism of the S_2 and S_1 electronic states of β -carotene. Non-totally symmetric modes efficiently couple the two surfaces and allow for vibrationally coherent (re)crossing between the states.

The spectra in Figure 6.7b suggest that most of the intense S_1 Raman bands

(290, 399, 1256, 1538, 1785 cm^{-1}) are candidates for tuning modes. The excitation pulse generates VC in totally symmetric modes that remain essentially unperturbed by the surface crossing. This interpretation is in line with the fundamental symmetry requirements for the B_u to A_g surface crossing encountered in the $S_2 \rightarrow S_1$ IC of β -carotene. Such a crossing must be mediated by vibrational modes of b_u -symmetry (Figure 6.10).¹⁹² The dramatic difference in the VC activity for numerous S_1 bands after IC (776, 1000, 1160, 1206, 1287, 1372, 1407 cm^{-1}), compared to the S_1 Raman spectrum is consistent with these modes being non-totally symmetric and therefore almost undetectable in conventional resonance Raman spectra (Figure 6.7b). In the experiments reported here, the VC evident in the $S_y \leftarrow S_1$ absorption window reports on the molecule in the vicinity of the surface crossing, that is, vibrationally hot molecules.¹⁹³ Here, S_1 and S_2 are strongly mixed allowing for both totally and non-totally symmetric modes to be Raman active and thus modulate the transient electronic signals. Such appearance of non-totally symmetric vibrations has been previously reported in time resolved anti-Stokes Raman experiments on 4-nitroaniline, although in an incoherent fashion.¹⁹⁴

Given that only symmetric modes are Franck-Condon active in the $S_2 \leftarrow S_0$ transition, VC in non-totally symmetric modes must, therefore, have been generated after photoexcitation. The high frequencies of many detected vibrations ($>1000 \text{ cm}^{-1}$) together with the 140 fs lifetime of S_2 firmly exclude impulsive generation of the VC by the surface crossing. Instead, the VC in non-totally symmetric modes must have been generated by anharmonic coupling with the originally excited symmetric modes.¹⁴⁹ Theoretically, one could differentiate between anharmonic coupling exclusively on S_2 and coupling strictly induced by the CI. Given the symmetry properties of the two states (B_u and A_g), however, such a differentiation appears largely semantic. The CI mixes the electronic and symmetry characters of the two states and, hence, strongly distorts the potential energy surfaces of S_2 and S_1 in its vicinity.

Although it is difficult to clearly assign the observed vibrations to coupling or tuning modes, we believe that the enhanced non-totally symmetric modes contribute to the coupling of S_2 and S_1 and, thereby, to the formation of the CI. VC in these modes is strongly affected by the CI, although in this case it is generation of VC rather than destruction by interference that has been predicted if a wave packet is already present in the coordinate prior to surface crossing.¹⁹⁰ The modes are fundamentally connected to the formation of the CI

because it is anharmonic coupling that generates the VC and the anharmonic coupling in turn is mediated by the CI. Non-totally symmetric modes exhibit the correct symmetry to couple the two electronic states and thereby mediate the breakdown of the Born-Oppenheimer approximation.¹⁹⁵ This notion is strengthened by our observation of long-lived surface re-crossings (Figure 6.8 and 6.10) that has been predicted to occur for both coupling and tuning modes.¹⁹⁰ It is vibrational cooling¹⁹³ that ultimately leads the system away from the vicinity of the CI and ensures complete IC into S_1 .

6.4 Outlook and Conclusion

In summary we are able to demonstrate that IC through a CI is vibrationally coherent. The precise coordinates underlying the vibronic surface coupling remain, however, unknown due to the computational complexity associated with quantum chemical studies of molecules as large as β -carotene. Recent advances in the generation of <10 fs UV pulses¹⁹⁶ should, however, allow us to extend our methodology towards smaller molecules such as the theoretically well studied pyrazine system where precise computational studies are feasible.^{197–203} The direct observation of VC therefore provides scope for the elucidation of the molecular coherent dynamics associated with electronic surface crossings and thus allows for direct insight into the basics behind the breakdown of the Born-Oppenheimer approximation for polyatomic molecules in the condensed phase. Even though the system only spends a short time at the position of the CI its effect on the VC is definite and should allow us to extract information on the structural parameters of this vibronic transition state.

Chapter 7

Population controlled impulsive vibrational spectroscopy

The technique and experiments described in this chapter were proposed by me. Both the experimental work as well as the data analysis was performed by Dr. Torsten Wende, Christoph Schnedermann and myself with all of us contributing to all experiments and the analysis of each individual experiment. The full chapter was written by myself but data and partial figures are reprinted with permission from Wende, T., Liebel, M., Schnedermann, C., Pethick, R.J., and Kukura P., *J. Phys. Chem. A*, **2014**, 118 (43), 99769984. Copyright 2014 American Chemical Society.²⁰⁴

7.1 Introduction

Time resolved vibrational spectroscopy has tremendously contributed to our understanding of chemical reaction dynamics on a molecular level.^{123,205–209} Frequency domain Raman techniques such as FSRS^{31,121} or coherent anti-stokes Raman spectroscopy (CARS)^{122,124} are capable of recording full vibrational spectra with temporal resolutions on the order of vibrational dephasing times.¹⁴⁸

In FSRS a so-called actinic pump pulse photoexcites the molecular system of interest, by means of two electric field interactions, and initiates a photochemical process (Figure 7.1a).²¹⁰ The narrow "Raman pump" ($\sim 15\text{ cm}^{-1}$, 1 ps) in combination with a short $\sim 15\text{ fs}$ probe pulse establishes VC which is subsequently probed by a second field interaction with the probe pulse. The signal is emitted into the probe direction and heterodyne detected as Raman gain on top of the probe spectrum. The frequency domain signal recorded is the

Fourier transformation of the initiated VC and other signal contributions, such as fluorescence, are necessarily integrated together with the Raman signal. Additionally, the long duration of the Raman pump enables many additional signal pathways due to time ambiguity with both the pump and the probe pulses. As a result, complicated Raman line shapes on top of often non-trivial backgrounds are commonly encountered.^{126,128} Despite these disadvantages FSRS has tremendously contributed to our understanding of ultrafast molecular dynamics and is a valuable technique for recording vibrational kinetics on the ultrafast time scale.^{29,126,175}

Instead of recording Raman spectra in the frequency domain it is possible to directly record them in the time domain.²¹¹ This approach was pioneered by the Tahara group^{25,129,212} but was, until recently, limited to the low frequency region ($<500\text{ cm}^{-1}$) of the vibrational spectrum.⁵¹ With the advent of BB-IVS, which can be regarded as a time domain analogue to FSRS, it is, however, possible to record Raman spectra over the full vibrational manifold of interest $<3500\text{ cm}^{-1}$. After photoexcitation with the actinic pump two field interactions with a short ($\sim 10\text{ fs}$) impulsive pump initiate VC which is subsequently probed by a broadband, WL, probe (Figure 7.1b). As in FSRS the signal is heterodyne detected on top of the WL spectrum, but now as VC that is directly recorded in the time domain by varying the impulsive to WL pulse delay. No time ambiguity is present due to the short duration and temporal separation of the actinic, impulsive and probe pulse. Additionally, unwanted signal contributions can be removed prior to Fourier transformation of the signal. These features allow for the acquisition of high-quality baseline free Raman spectra, over the full vibrational manifold of interest, as demonstrated in Chapter 4.

Both FSRS and BB-IVS suffer from the fact that not only molecules from the excited electronic state of interest but also solvent and ground state molecules contribute to the Raman spectra recorded. To isolate the pure excited state contribution complicated, and possibly error prone, subtraction of undesired spectral features has to be performed.

In Chapters 5 and 6 we employed population controlled impulsive vibrational spectroscopy (pc-IVS) to isolate excited state VC. A short pump ($\sim 10\text{ fs}$) resonantly excites a molecular system and simultaneously initiates VC on the excited electronic state. A long (200-1000 fs) dump pulse, time coincident with the pump but only resonant with an electronic transition from the excited electronic state removes part of the generated population.^{149,167} As the dump

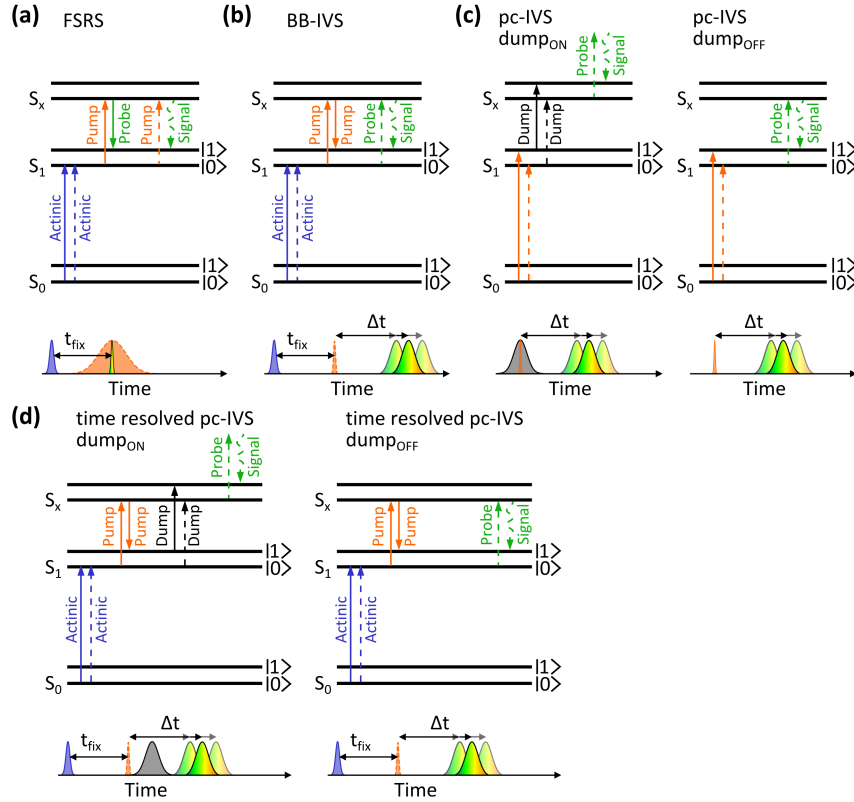


Figure 7.1: **Energy ladder diagrams for some nonlinear Raman processes.** (a) Diagram for femtosecond stimulated Raman spectroscopy (FSRS). (b) Diagram for broadband impulsive vibrational spectroscopy (BB-IVS). (c) Diagram for population controlled impulsive vibrational spectroscopy (pc-IVS). Probe interactions in the presence (dump_{ON}) and absence (dump_{OFF}) of the dump electric fields are indicated. (d) Diagram for time resolved population controlled impulsive vibrational spectroscopy. Probe interactions in the presence (dump_{ON}) and absence (dump_{OFF}) of the dump electric fields are indicated.

pulse is temporally long compared to common vibrational periods the two field interactions generate VC that is not observable in an ensemble averaged measurement (Figure 7.1c). The difference between the VC detected in the absence and presence of the dump pulse thus only contains VC contributions from the excited electronic state.

In this Chapter we combine BB-IVS with pc-IVS which allows us to record background and baseline free vibrational kinetics of excited electronic states (Figure 7.1d).

7.2 Experimental and results

The actinic pulse triggers the phototransformation by electronic excitation of ground state molecules. After a given time delay VC is generated by the impulsive pump which has to be off-, or pre-resonant with electronic transitions from the ground electronic state to exclude excited state VC generation by photoexcitation. We probe the VC evolution as a function of WL probe to impulsive pump delay as in all previous experiments. To implement the pc-IVS scheme we introduce a dump pulse which is temporally delayed with respect to the impulsive pulse. Again, the dump pulse is only resonant with electronic transitions from the excited electronic state. Following the action of the impulsive pump, and hence VC generation, the dump rises and depletes excited state population and with it some of its VC (Figure 7.1d and 7.2).

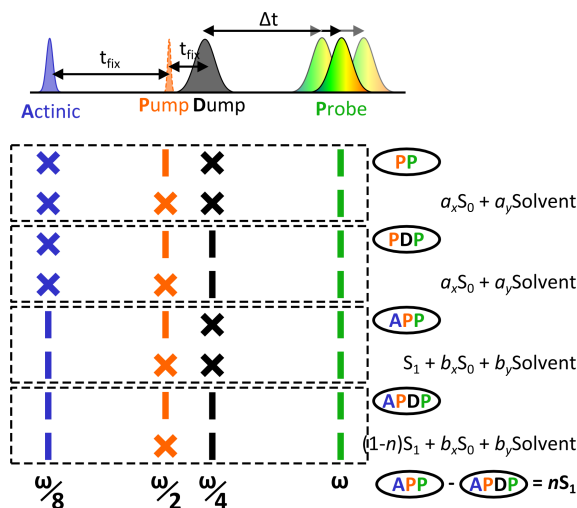


Figure 7.2: Chopping scheme for time resolved pc-IVS. Crosses represent blocked and lines unblocked beams. The direct comparison of the VC contributions of the APP and APDP experiments isolates pure excited state VC.

We employ a triple chopping scheme and record four different signals (Figure 7.2). The impulsive pump-probe (PP) experiment can be regarded as a TA experiment with the excitation pulse being off-resonant with any electronic transitions from the ground electronic state. As a result only VC in solvent and ground state molecules is impulsively excited. In the impulsive pump-dump-probe (PDP) scheme the dump pulse acts after the impulsive generation of VC in ground state and solvent molecules. As the dump is off-resonant with all transitions from populated electronic states, however, it does not alter the

VC content of the experiment. PP and PDP experiments should thus contain identical VC contributions and a comparison between the two allows for the identification of possible artefacts which might be introduced by, for example, temporally overlapping impulsive and dump pulses, pre-resonant impulsive pump pulses or the excessive use of dump power.

In the presence of the actinic pump we perform the actinic-impulsive pump-probe (APP) and the actinic-impulsive pump-dump-probe (APDP) experiments. The former is identical to PP but in the presence of excited electronic state population. VC in solvent, ground and excited states is therefore generated by the action of the impulsive pulse. In the APDP experiment the dump pulse depletes excited state population and hence destroys the respective VC. As a result, the direct subtraction of APP and APDP isolates excited state only VC. Previously, in BB-IVS, it was necessary to employ a rather complex subtraction scheme and, additionally, record pure solvent VC in order to extract an excited state Raman spectrum from the combination of PP and PDP (Chapter 4). The introduction of the dump pulse, however, eliminates all computational post-processing. Even though the use of a total of three choppers might seem rather complex it is possible to remove all but one chopper to directly record pure excited state VC on top of an electronic background. The signal recorded by modulating only the dump pulse, at half the laser repetition rate, is equivalent to the APP minus APDP experiment and hence pure excited state VC.

Time resolved pc-IVS of *trans*-stilbene

To demonstrate the capabilities of time resolved pc-IVS for recording high quality Raman spectra we employ *trans*-stilbene (Figure 7.3) as a well studied benchmark system for Raman spectroscopy.^{182,213–216} The S_1 state of *trans*-stilbene possesses a solvent dependent excited state lifetime of ~ 100 ps due to the presence of a reaction barrier on the IC, or reaction, coordinate.^{217,218}



Figure 7.3: Structure of *trans*-stilbene.

We excite *trans*-stilbene dissolved in toluene ($\text{OD} = 1.0$ in a $200\text{ }\mu\text{m}$ flow cell) with a 200 fs actinic pulse centered at 325 nm resulting in a maximum differential ESA signal of 100 mOD. After a variable actinic to impulsive pump time delay we initiate VC using a 9.0 fs impulsive pump centered at 550 nm and probe the temporal evolution with a broadband WL probe. Differential absorbance maps are acquired over a total of 1.8 ps of impulsive pump-probe delay with 40 ms integration time per time point. We isolate the VC from the differential absorbance map after correcting for WL chirp, truncating at $\Delta t = 100$ fs and removing the electronic kinetics by exponential fitting (see Chapter 3 and 4 for details).

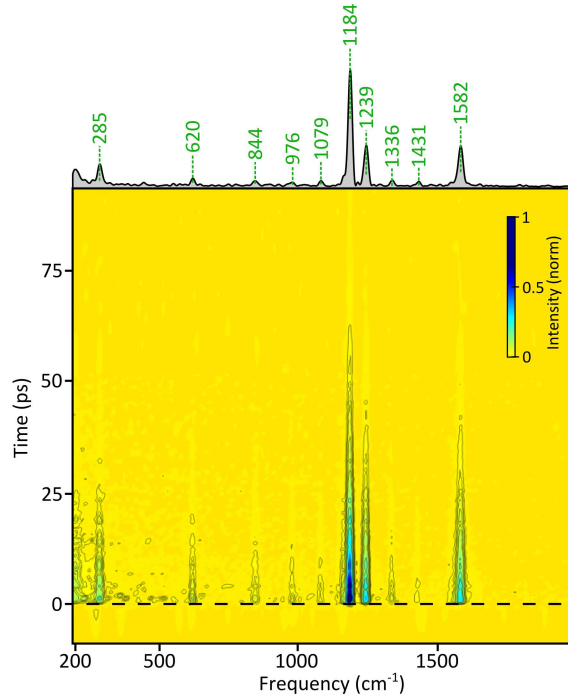


Figure 7.4: Vibrational kinetics of the S_1 electronic state of *trans*-stilbene dissolved in toluene. Inset is a spectrum recorded at $t=5$ ps indicating the major bands contributing to the spectra. A total of 150 spectral time points are recorded. The experimental parameters are: WL, $44\text{ }\mu\text{m}^2$ focus (at FWHM), 2 nJ; dump, $80\times 75\text{ }\mu\text{m}$ focus (at FWHM), 160 nJ; actinic, $60\times 80\text{ }\mu\text{m}$ focus (at FWHM), 60 nJ; impulsive pump, $65\times 60\text{ }\mu\text{m}$ focus (at FWHM), 90 nJ.

To extract the S_1 VC contributions we employ 160 nJ of a 200 fs dump pulse centered at 515 nm which rises immediately after the action of the impulsive pump. The difference between the VC obtained for the APP and APDP experiments solely contains S_1 VC. We generate Raman spectra as a function of

actinic to impulsive pump delay by averaging the Fourier intensity spectra over the 540-690 nm spectral region (Figure 7.4).

A representative Raman spectrum at an actinic to impulsive pump delay of 5 ps shows good agreement with previously reported frequencies^{182,216} (Figure 7.4 inset) but the spectral intensities deviate. These differences are most likely a result of different resonance conditions in combination with the temporal resolution induced decrease in high frequency VC amplitude.

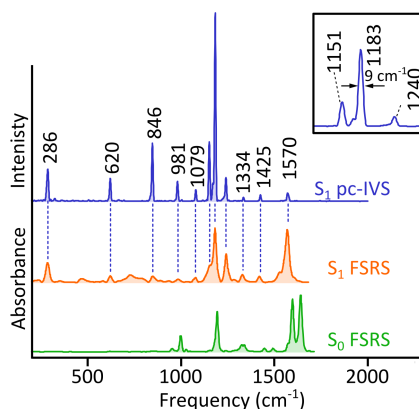


Figure 7.5: S_1 Raman spectra of *trans*-stilbene dissolved in cyclohexane recorded via FSRS (orange) and pc-IVS (blue) as well as a S_0 FSRS spectrum for comparison. The FSRS spectra are reproduced with permission from:¹⁸² Dobryakov, A. L., Ioffe, I., Granovsky, A., Ernsting, N., Kovalenko, S. A. *J. Chem. Phys.* **137**, 244505-1 (2012), <http://dx.doi.org/10.1063/1.4769971>. Copyright 2012, AIP Publishing LLC.

To allow for a better comparison with the, to our knowledge, best Raman spectrum of *trans*-stilbene reported thus far¹⁸² we exchange the solvent from toluene to cyclohexane (*trans*-stilbene OD = 0.8). By integrating over a impulsive pump-probe delay range of 4.8 ps we reduce the linewidth of the Fourier intensity spectrum shown in Figure 7.5, a task that would require additionally spectral narrowing of the Raman pump in FSRS.^{134,219} The comparison of the time resolved pc-IVS to the FSRS spectrum shows overall satisfactory spectral agreement. Some bands are, however, absent in our measurement as for example in the 650 cm^{-1} spectral region. Most of these differences are probably caused by different resonance conditions. We resonantly excite and probe the S_1 VC (500-650 nm) while Dobryakov *et al.* used a 645 nm Raman pump. We note that a shift of only 20 nm (645 to 625 nm) of the Raman pump frequency in FSRS measurements resulted in notable changes in the overall appearance

of the spectra^{182,216} and our deviations are thus not surprising. As a distinct advantage, however, we can firmly exclude the presence of bands caused by baseline or spectral subtraction artefacts in the pc-IVS experiment.

Time resolved pc-IVS of retinal protonated Schiff base

As mentioned previously *trans*-stilbene is an ideal benchmark system as high quality frequency domain Raman spectra are readily available for comparison. To demonstrate the distinct advantages of time domain detection of the VC we chose all-*trans* n-butyl retinal protonated Schiff base (nBu-RPSB). Previous attempts to record FSRs spectra of the temporal evolution of the RPSB chromophore containing protein bR, after photoexcitation, were hampered by the presence of strongly dispersive line shapes.¹²⁶ These line shape distortions could be explained by a process termed Raman initiated by nonlinear emission (RINE), a process that occurs if the Raman pump and probe pulses are resonant with a SE transition. In RPSB containing systems unfavourable resonance conditions can hardly be avoided as SE or ground state absorption transitions are present throughout the UV to NIR spectral regions¹⁵³ thus rendering frequency domain experiments very difficult.

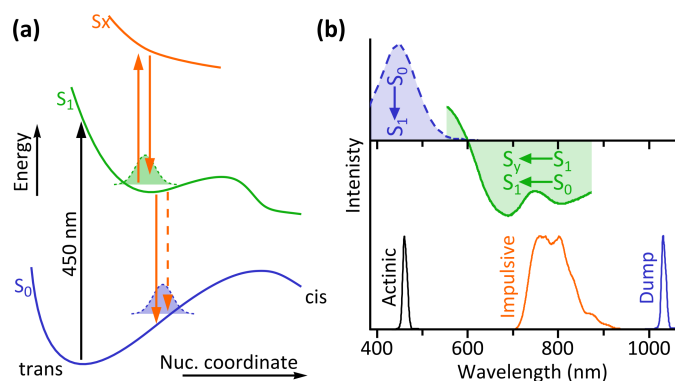


Figure 7.6: **Experimental parameters for time resolved pc-IVS of nBu-RPSB.** (a) Schematic of the energetically lowest potential energy surfaces of nBu-RPSB. The impulsive pulse (orange) generates S₁ VC as well as S₀ VC through the SE transition from S₁. (b) Ground state absorption spectrum (blue, dashed) and electronic transient composed of SE and ESA bands after photoexcitation (green) of nBu-RPSB and spectra of the actinic (black), impulsive (orange) and dump (blue) pulses employed in the experiment. The experimental parameters are adjusted to: WL, 45 μm^2 focus (at FWHM), 2.5 nJ; impulsive pump, 56 μm^2 focus (at FWHM), 90 nJ; actinic pump 70x90 μm^2 focus (at FWHM), 300 nJ; dump, 100 μm^2 focus (at FWHM), 230 nJ;

Figure 7.6a shows a schematic of the PES of nBu-RPSB. We populate the S_1 electronic state by photoexcitation of nBu-RPSB dissolved in methanol (OD = 1 in 200 μm), with an actinic pump centered at 450 nm (200 fs) (Figure 7.6b). ESA and GSB signatures are present in the spectral region <600 nm and in the NIR we observe a $S_0 \leftarrow S_1$ SE transition. The characteristic double hump of the SE band is indicative of a superimposed ESA feature.

To generate VC we employ 90 nJ of a 10 fs impulsive pulse covering the 700-930 nm spectral region. Due to the unfavourable resonance conditions we not only generate VC on S_1 and S_0 via impulsive stimulated Raman scattering but also on S_0 via the SE transition (Figure 7.6a). The latter process is very efficient as the VC generation is directly coupled to the electronic transition.

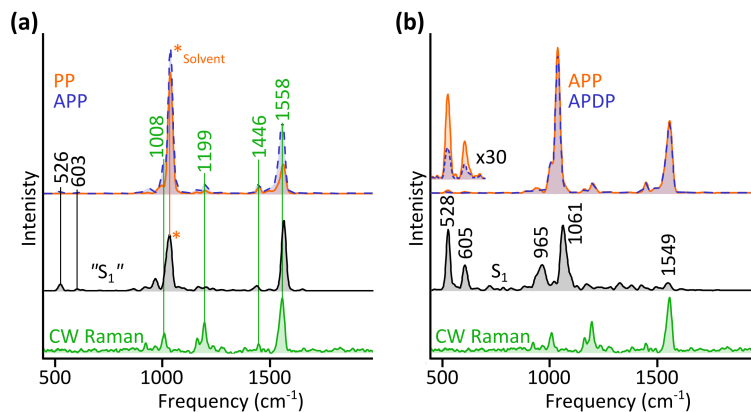


Figure 7.7: **Time resolved pc-IVS of all-*trans* nBu-RPSB.** (a) Comparison of the Raman spectra recorded for nBu-RPSB dissolved in methanol for the APP (orange) and PP (blue, dashed) experiments. Algorithm based subtraction of PP from APP yields a spectrum (black) that is strongly contaminated by both S_0 (green lines) as well as solvent (orange line) residuals. Some S_1 bands are, however, present as indicated in black. (b) Direct subtraction of the Raman spectra recorded for APDP (blue, dashed) and APP (blue, dashed) yields a clean S_1 spectrum (black) as highlighted by direct comparison to a spontaneous ground electronic state Raman spectrum (green).

The enhanced VC generation probability manifests itself if we compare spectral averages of the 745-830 nm spectral region. In the presence of the actinic pulse, and hence fewer S_0 molecules, the intensity of the S_0 bands at 1008, 1199, 1446 and 1558 cm^{-1} increases due to S_0 VC generation via the SE transition (Figure 7.7a). As an additional complication, we expect different Raman cross sections for VC generation via SE or impulsive stimulated Raman scattering. The algorithm based subtraction of the VC recorded for PP and APP thus fails

to reveal S_1 bands but is instead heavily contaminated by ground state and solvent contributions as evidenced by comparison to a ground state spontaneous Raman spectrum (Figure 7.7a). Some S_1 frequencies, as for example at 527 and 604 cm^{-1} are, however, present in the spectrum albeit at very low intensities. In summary, the BB-IVS technique fails to retrieve an S_1 spectrum and application of the dump pulse is necessary in order to isolate a representative excited state spectrum.

The dump pulse centered at 1030 nm (~ 200 fs, 230 nJ) tuned into electronic resonance with the SE transition removes 20% of the excited state population and with it VC from S_1 . A spectral comparison of the APP and APDP experiments shows that the 527 and 604 cm^{-1} bands previously assigned to VC originating from S_1 decrease in intensity upon action of the dump pulse. The dominant S_0 and solvent features, however, remain unaffected. A direct subtraction of APDP from APP reveals the pure S_1 spectrum of nBu-RPSB (Figure 7.7b). The high intensity S_0 bands at 1558 and 1008 cm^{-1} , as well as the methanol peak at 1037 cm^{-1} , are completely eliminated from the spectrum and new bands at 528, 605, 965, 1061 and 1549 cm^{-1} dominate the spectrum.

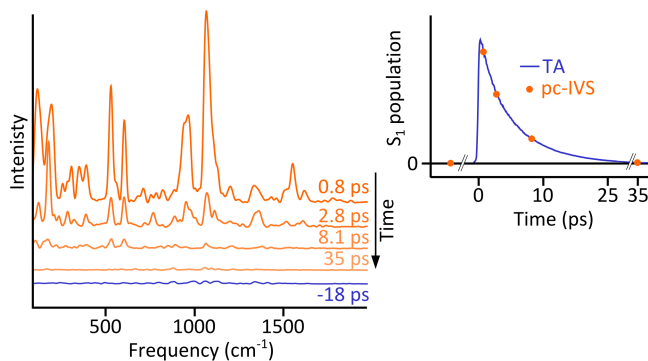


Figure 7.8: Vibrational kinetics, obtained via time resolved pc-IVS, of the S_1 electronic state of nBu-RPSB as a function of actinic to impulsive pump delay (orange). The pre time zero baseline is shown in blue. Inset: Comparison of the S_1 population decay recorded via transient absorption (blue line) to the mean amplitude of the major vibrational bands of the S_1 spectrum (orange dots).

To verify the spectral origin of these bands we record S_1 Raman spectra at varying actinic to impulsive pulse delays. At negative time delays no Raman intensity is detected in the time resolved pc-IVS experiment (Figure 7.8). Following photoexcitation we observe the rise of the previously reported spectrum which decays with increasing actinic to impulsive time delay. A comparison of

the mean spectral amplitude of the major Raman bands to the decay of the SE signal shows remarkably good agreement and hence verifies that we are indeed observing Raman spectra originating from S_1 .

Time resolved pc-IVS of low concentration astaxanthin

We perform time resolved pc-IVS experiments on the carotenoid astaxanthin (AXT) dissolved in dimethyl sulfoxide (DMSO) (Figure 7.9a) to showcase some limitations and possible sources of artefacts at low signal levels. AXT is found in *Homarus americanus* and *Homarus gammarus* in both free and aggregated form or bound in the proteins α - and β -crustacyanin. It is responsible for the greenish-blue colour of these lobsters.^{220,221} Upon boiling a lobster AXT is released from the proteins and the cooked lobster turns red.²²²

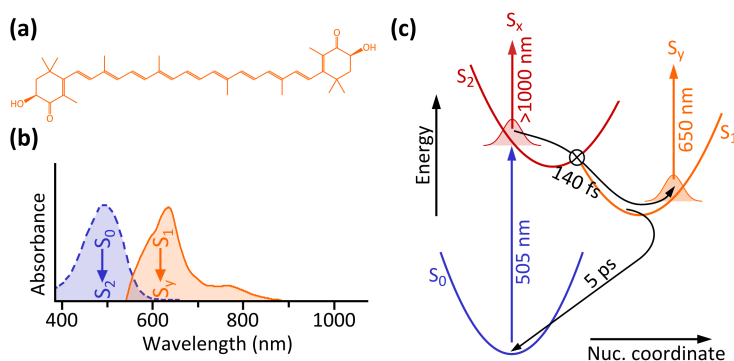


Figure 7.9: **Astaxanthin, structure and photophysics.** (a) Structure of astaxanthin (AXT). (b) One-photon absorption spectra of the S_0 and S_1 electronic states of AXT. (c) Potential energy scheme of AXT.

From a spectroscopic perspective AXT behaves similar to β -carotene.^{130,223} The absorption spectra of AXT is, however, slightly red shifted, compared to β -carotene (compare Figures 7.9b and 6.1). Photophysically, the systems are almost identical with only small difference in spectral positions and decay constants (compare Figures 7.9c and 6.1). Direct $S_1 \leftarrow S_0$ excitation is forbidden by symmetry and the lowest one-photon allowed transition is into S_2 . S_2 rapidly internally converts into S_1 (~ 140 fs) which subsequently relaxes back into S_0 with a time constant of ~ 5 ps.²²³

We employ a solution of AXT dissolved in DMSO at an optical density of 0.25 (in a 200 μm flow cell) and excite the molecules using a 200 fs actinic pulse centered at 515 nm. The maximum S_1 ESA signal is 20 mOD, which is

~ 10 times lower than commonly employed signal levels. To initiate VC we use 20 nJ of a 10.0 fs impulsive pump centered at 800 nm. A comparison of the VC activity recorded for APDP and APP at a 2.5 ps actinic to impulsive pulse delay, generated by averaging the Fourier amplitude spectra in the 625-675 nm spectral region, is shown in Figure 7.10a. The strong DMSO band at 670 cm^{-1} dominates the spectrum, with all other contributions being more than one order of magnitude smaller. Upon computing the difference between the spectra we retrieve the S_1 spectrum of AXT which still shows a band at 670 cm^{-1} . This band might be caused by spectral leakage.

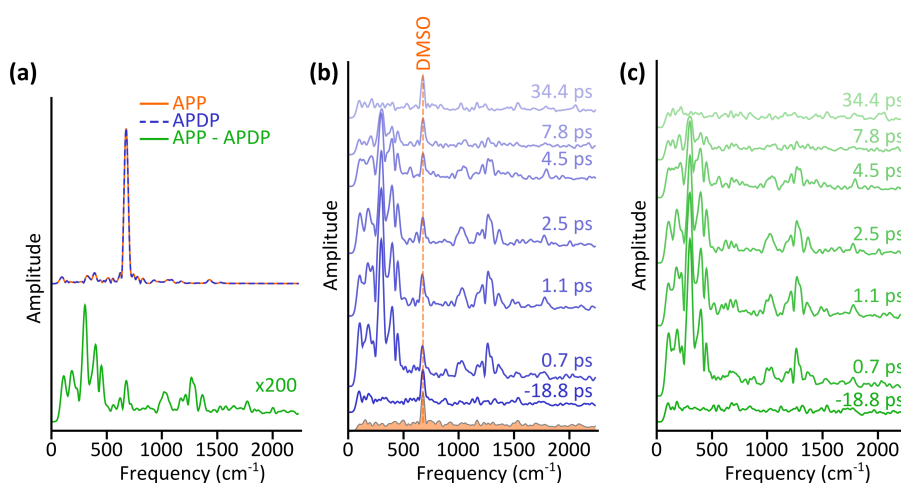


Figure 7.10: **Time resolved pc-IVS of astaxanthin at low signal levels.** (a) Raman spectra recorded for APP (orange) and APDP (blue, dashed) at an actinic to impulsive pump delay of 2.5 ps. The difference between the two spectra is shown in green (time domain subtraction). (b) Temporal evolution of the Raman activity of S_1 (blue), extract as APP minus APDP. Comparison to a spectrum obtained as PP minus PDP (orange) shows that DMSO contamination is present (orange line). (c) Algorithm based subtraction of the VC recorded for PP minus PDP from the APP minus APDP VC isolates clean S_1 spectra. Foci are adjusted to: WL, $47\text{ }\mu\text{m}^2$ (at FWHM); impulsive pump, $55\text{ }\mu\text{m}^2$ (at FWHM); actinic pump, $80\text{ }\mu\text{m}^2$ (at FWHM); dump, $80\text{ }\mu\text{m}^2$ (at FWHM). 80 nJ of a 300 fs dump pulse centered at 720 nm is used.

To identify possible artefacts in the S_1 spectrum we record multiple spectra at different actinic to impulsive pulse delays, as previously done for nBu-RPSB. Most of the spectral features decay with increasing time delay. The 670 cm^{-1} mode, however, seems to be growing and is even present before AXT has been electronically excited (Figure 7.10b). A growing band can be rationalised as follows: The impulsive pump is resonant with the S_1 ESA. As S_1 de-

cays less pump photons will be absorbed and hence more photons are available to generate VC in off-resonant molecules. This observation suggests that the interaction with the dump pulse weakly effects VC in off-resonant molecules. If the magnitude of the off-resonant contribution in the initial spectrum is much larger than those of the electronic state of interest this weak perturbation can manifest itself as spectral leakage and APP minus APDP no longer yields a clean spectrum.

Fortunately, we are able to directly quantify the extend of spectral leakage by computing the difference between the PP and the PDP experiment. Here, no excited electronic state is generated by the actinic pulse and hence only the spectral leakage will be present in the difference spectrum. The PP minus PDP spectrum shown in Figure 7.10b verifies that the 670 cm^{-1} mode indeed contaminates the S_1 spectra.

With the subtraction algorithm introduced, for BB-IVS, in Chapter 4, we should be able to remove all spectral leakage and hence recover clean spectra. We compute the VC for PP minus PDP and subtract it from the VC obtained for APP minus APDP by using the subtraction algorithm. Figure 7.10c shows the spectra obtained after subtraction. The contaminations are successfully removed and we are left with pure S_1 spectra which decay in agreement with the electronic lifetime of S_1 .

7.3 Conclusion and Outlook

We combined BB-IVS with the concept of population control to record vibrational kinetics of excited electronic states without the need for computational subtraction of spectral contributions from ground state or solvent molecules.

In its original form time resolved pc-IVS requires a total of three choppers which is experimentally challenging to implement but allows for the identification of possible artefacts and their removal, as demonstrated on AXT at low signal levels. At higher concentrations two of the choppers can be removed from the system and the VC of interest is directly recorded as APP minus APDP by modulating only the dump pulse.

One of the disadvantages of time domain techniques is that the probe pulse has to be translated in time which is a slow process compared to most laser repetition rates. Despite this limitation we achieve experimental times which are comparable to, for example, FSRS. The proof of principle experiments on

trans-stilbene is performed at a maximum S_1 ESA signal of 100 mOD with acquisition times of 25 s per spectrum. Dobryakov *et al.*¹⁸² employed a maximum S_1 ESA signal of 200 mOD and integrated for 12-36 s per time point which, after correcting for the higher signal magnitude, is comparable to, or worse, than our experimental parameters.

Beyond experimental and signal considerations the time domain approach outperforms frequency domain based Raman techniques in terms of background and baseline problems. The possibility to remove electronic signal contributions prior to Fourier transformation eliminates all baseline related artefacts and, as demonstrated on nBu-RPSB, systems with complex resonance structures are readily accessible with time resolved pc-IVS.

In summary we believe that time domain Raman spectroscopy in the form of time resolved pc-IVS is the currently best available technique for recording high quality vibrational kinetics of any molecular system of interest.

Chapter 8

On quantum coherent control in the one photon limit

8.1 Introduction

Following photoexcitation molecules can react via multiple pathways and, as a result, form different photoproducts. For example, if the all-*trans* RBSP chromophore is excited photoisomerisation might occur at different positions along its backbone and multiple *cis* isomers are formed. Each of these possibilities is associated with a certain probability which is determined by the underlying PES of the molecule. Coherent control (CC)^{224–229} aims at manipulating the PES dictated photoreaction probabilities by specifically designing electric control fields.

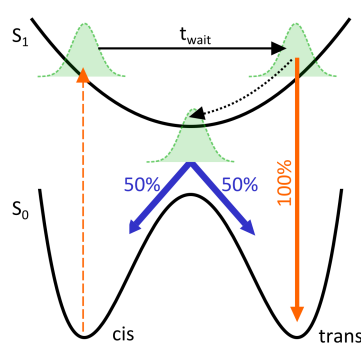


Figure 8.1: The Tannor-Rice scheme illustrated for an isomerisation reaction. The excitation pulse (orange, dashed) generates excited state population that is, after a waiting time (t_{wait}), coherently transferred to the photoproduct state by employing a second pulse (orange, solid).

One approach to achieving CC is the so-called Tannor-Rice scheme^{230,231} il-

illustrated in Figure 8.1. A photoisomerisation reaction is triggered via a $\pi^* \leftarrow \pi$ excitation with a short laser pulse. The molecules start evolving on the excited electronic state PES and, at a specific time delay later, a second photon interacts with the molecules and coherently transfers the excited state population into the desired product state. As a result a much higher isomerisation yield is achieved as compared to the uncontrolled process. Another CC approach named after Brumer-Shapiro²³² relies on quantum interference between multiple reaction pathways. By photoexciting a molecule into a superposition of different states the branching ratio into specific product channels can be controlled. Both of these theoretically proposed control schemes have been demonstrated experimentally.^{233–235}

Early experimental approaches to CC were guided by knowledge about the PES structure of the relatively simple systems under study. For larger molecules information about the PES is unfortunately limited and the implementation of CC based on chemical intuition is therefore challenging.²³⁶ One way to circumvent this problem is to implement a feedback loop guided search for optimal control fields.^{237–241} Experimentally, such a feedback loop can be implemented by combining a pulse shaper with a genetic algorithm (GA).²⁴² Rather than knowing the optimal control field(s) the GA generates a set of random guesses that are experimentally evaluated by, for example, measuring the transient signal of the desired target state.^{239,240} After determining the relative performance of the individual guesses an improved set of parameters is generated and the process is repeated until an optimum control field is determined.²⁴³ Even though such a blind optimisation might, at first, appear hopeless due to the possible presence of many local control maxima on complicated PESs it has been shown that each control maximum corresponds to a global maximum²⁴⁴ and the application of a GA is thus a solid approach towards CC.

The control scenarios discussed thus far are relying on strong electric fields, that is, more than one photon is utilised for coherently controlling the outcome of the photochemical process. Recently, Prokhorenko *et al.* reported impressive CC results in the weak field (WF) or one-photon limit²⁴⁵ with excitation levels as low as one photon per one hundred molecules. The authors performed GA guided CC experiments on bR and reported control over the outcome of the photoisomerisation reaction by $\pm 20\%$ by shaping both phase and amplitude of the excitation pulse. Similar results were obtained for the laser dye rhodamine

101 (RHO101).^{246,247} According to the authors, the population transfer efficiency from the ground to the excited electronic state could be controlled by 30%. Both experiments showed evidence for the possibility to influence the outcome of the photochemical process by pure phase shaping, $\pm 6\%$ in bR and $+6\%$ in RHO101.

The observation of WF phase only (WFPO) CC sparked a controversy^{248,249} which has mainly been addressed theoretically. In a closed quantum system WFPO is impossible but could be feasible in an open quantum system if certain criteria are met.^{236,250–255} A shaped vibrational wavepacket could be able to influence the outcome of the photochemical process if a favourable dissipation, or dephasing, mechanism is present. In the Tannor-Rice CC picture we rationalise this possibility by replacing the second pulse by an environmentally governed dephasing mechanism that traps the shaped wavepacket in the desired photoproduct state.²⁵¹ If dephasing is indeed crucial then systematic tuning of the latter should allow us to drastically influence the amount of achievable WFPO CC.

Based on the WFPO results reported on bR we design an experiment to test this prediction. A comparison between bR, rhodopsin (rho)¹¹⁶ and isorhodopsin (isorho)^{256,257} should allow us to explore very different dephasing contributions in comparable systems, that is, an RPSB molecule embedded in a protein pocket. The chromophore is in the all-*trans*, 11-*cis* or 9-*cis* configuration for bR, rho and isorho, respectively. Both bR and rho exhibit the same photoisomerisation yield of 65%^{156,173} but the latter isomerises approximately three times faster (500 vs 200 fs)^{117,256} and we therefore expect that the role of dephasing for WFPO CC will differ considerable between these systems. A comparison between rho and isorho allows us to directly compare two chromophore embedded in the same opsin environment. Both rho and isorho form the same photoproduct, batho-rhodopsin,²⁵⁸ but the photoisomerisation rate is slower (600 fs) and less efficient (22% quantum yield) in the latter. Additionally, recent work suggests that isorho might be an ideal candidate for CC experiments.²⁵⁹ Taken together, a comparative experimental study between these systems should allow us to unravel the role of dephasing in WFPO CC, a question that is difficult to address theoretically as detailed knowledge of the PES and dephasing channels is necessary.

8.2 Experimental results

Pulse shaping considerations

The experimental implementation of WF CC is illustrated in Figure 8.2a. A complex electric field excites the molecular system of interest and generates a vibrational wavepacket. This wavepacket should enhance, or suppress, the generation of the desired photoproduct compared to a TL pulse. An initially TL pulse is manipulated by means of a pulse shaper such as an SLM or an acousto-optical modulator.⁸⁶ As pointed out previously, if polyatomic molecules are employed the PES is often unknown and a GA is used to generate random electric field guesses. The synthesised pulses photoexcite the system and the amount of generated photoproduct is measured, in this example with a probe pulse (Figure 8.2b). To measure the CC performance the product yield obtained is compared to the one obtained with a TL pulse. After evaluating all initial fields the GA generates a new set of pulses and, after several iterations, the optimum control pulse is identified.²⁴⁴

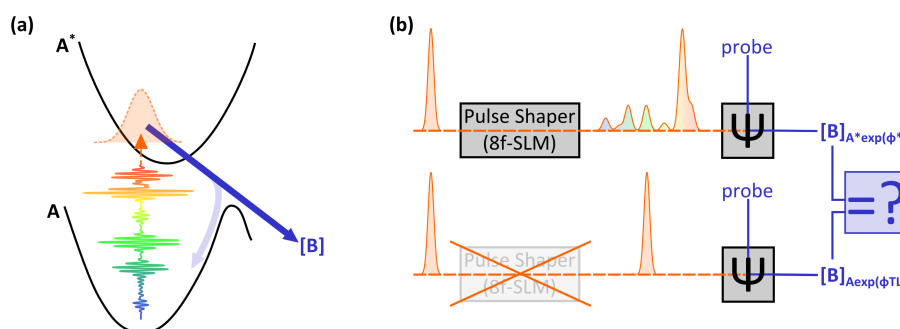


Figure 8.2: **Concept of one photon coherent control.** (a) A specifically designed electric field photoexcites a molecular system. The information encoded in the excitation field results in enhanced formation of photoproduct B. (b) Experimental implementation of a feedback loop guided CC experiment.

The implementation of this WF CC approach is unfortunately very complicated as underlined by the fact that only the Miller group reported successful experiments thus far.^{245,246} To access the full shaping space it is necessary to modulate both the phase and the amplitude of the field. A double pulse, for example, requires both phase and amplitude terms. As a result of the amplitude changes each synthesised electric field will excite a different amount of molecules, irrespective of the presence of CC. To distinguish the amplitude

effect from CC induced changes in photoproduct formation the amount of photons absorbed by the sample have to be precisely determined. Once normalised for this value the effect of CC is evaluated by the GA.

Experimentally, this normalisation is possible if both the sample absorbance as well as the excitation pulse spectrum can be accurately measured. Even the slightest calibration errors in the wavelength axis of the spectrometer, grating and detector quantum efficiencies or spatial chirp in the pump or probe pulses might deteriorate the normalisation quality. This problem is amplified by the GA which optimises the normalised signal. If a miss calibration is present the GA will optimise towards the calibration error which could be mistaken for successful CC. Additionally, a CC approach based on computational normalisation is incapable of accounting for shaping induced spatio-temporal coupling.^{90–92} As demonstrated previously, if a mask is applied to a pulse-shaper operated in 4f-configuration the beam path is altered which can result in severe beam displacements at the sample position (see Figure 3.12b).⁹² Even if this problem is reduced by operating in double pass, or 8f operation, minor effects of shaping induced spatio-temporal coupling are still present.

Self-referenced weak field coherent control

We propose a WF self-referenced CC (SRCC) experiment that circumvents the artefact prone normalisation procedure and directly measures the CC performance (CC_{target}). After synthesising the electric control field with an SLM (Jenoptik SLM-S320d), integrated into an 8f-grating stretcher, we generate two identical pulse copies with a 50:50 beamsplitter (Figure 8.3). One of the pulses ($E_{reference}$) passes through an 8 cm BK7 glass rod and accumulates a considerable amount of chirp. The second pulse ($E_{control}$) remains unmodified. Both beams are then focused into the same sample, but at different positions, and the generation of photoproduct in the target state is evaluated for both pulses simultaneously by measuring a differential absorbance signal. The ratio between these two measurements (CC_{target}) should directly reveal the amount of control.

To validate the SRCC approach we consider an initially TL ~ 20 fs pulse as shown in Figure 8.4a. Upon passing through the glass rod $E_{reference}$ is chirped to ~ 1.5 ps as highlighted by its Wigner representation and the associated temporal envelope (Figure 8.4b). We generate a 55 fs spaced pulse train as an example for a possible control field and compare the result obtained for $E_{control}$

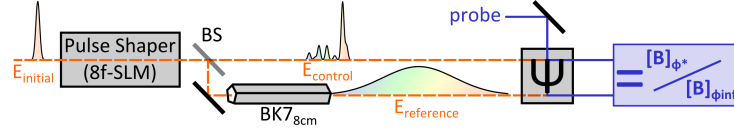


Figure 8.3: Implementation of the self-referenced CC (SRCC) experiment. The transform limited pulse ($E_{initial}$) is shaped by an 8f-SLM and then split into two identical copies with a 50:50 beamsplitter (BS). One of the two electric fields ($E_{reference}$) is strongly chirped by passing through an 8 cm BK7 glass rod. The CC performance (CC_{target}) is evaluated as the ratio of simultaneously performed, but individual, experiments with either the chirped reference ($E_{reference}$) or the unchirped pulse ($E_{control}$).

and $E_{reference}$ (Figure 8.4c). The temporal envelope of the former pulse shows the expected pulse train structure while the latter exhibits strong linear chirp and an overall very different temporal behavior. Importantly, the bandwidth of 1500 cm^{-1} (550-600 nm) remains linearly chirped. To electronically excite a molecular system two electric field interactions have to occur during the electronic dephasing time which is commonly around 30-50 fs at room temperature. This timescale in combination with the linear chirp of $E_{reference}$, therefore limits the available bandwidth for vibrational wavepacket generation to $\sim 30\text{-}50\text{ cm}^{-1}$. $E_{control}$, on the other hand, has its full bandwidth available. Given these considerations we believe that the strongly chirped $E_{reference}$ field serves as a good reference pulse for the no-control assumption but note that even if $E_{reference}$ was to exhibit some control over CC_{target} it would differ dramatically from $E_{control}$ and GA convergence should thus be observed.

Performance of self-referenced coherent control

To estimate the sensitivity of SRCC we perform an experiment on the laser dye rhodamine 101 (RHO101) dissolved in methanol at an OD of 0.7 in a $200\text{ }\mu\text{m}$ flow cell. A 16 fs pulse centered at 576 nm (9.1 nJ) excites RHO101 and the SE signal in the 620-680 nm spectral region is recorded at a pump-probe delay of 30 ps using a WL probe pulse. The signal level at the peak of the SE band is $-7.27 \pm 0.09\text{ mOD}$. The excitation level is $\frac{7.27}{700} \sim 1$ out of 100 molecules. We generate random amplitude masks with the SLM to induce strong signal fluctuations in the $E_{control}$ and $E_{reference}$ channels and compare it to CC_{target} normalised to the signal level of $E_{control}$ without amplitude modulation (Figure 8.5a). Over a period of 30 min, the time scale of a typical SRCC experiment, we observe no

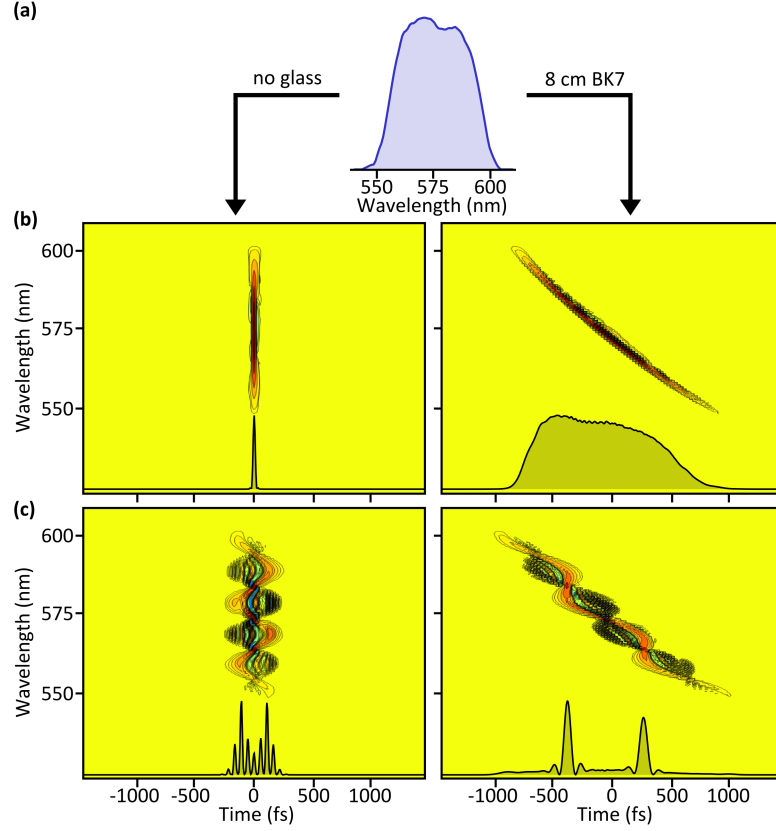


Figure 8.4: **Simulated electric fields for SRCC.** (a) Spectrum of the initial pulse. (b) Comparison of the Wigner representations and temporal envelopes for a TL $E_{control}$ (left) and a strongly chirped $E_{reference}$ (right) electric field. (c) Comparison of the Wigner representations and temporal envelopes for $E_{control}$ (left) and $E_{reference}$ (right) after generation of a pulse train with 55 fs spacing. The spectral content of all electric fields shown in the Wigner representation is identical to (a).

drift in CC_{target} and achieve a signal stability of $90 \mu OD$ within 100 ms integration time (95 % confidence interval). The histograms of CC_{target} highlights a signal spread close to shot-noise limit behavior (Figure 8.5b). From a signal to noise perspective the system is thus suitable for the WF SRCC experiments as even small changes in the CC_{target} magnitude $<1\%$ should be detectable. We note that the GA should even converge towards optimisation targets below the signal to noise ratio due to the resulting shift in the mean of the distribution of CC_{target} . The rate of convergence, however, will be considerably reduced.

Prior to performing WF SRCC we benchmark the performance of the GA with a high field CC experiment by increasing the pump power to an SE signal magnitude of -146 mOD (165 nJ). Here, more than one photon can inter-

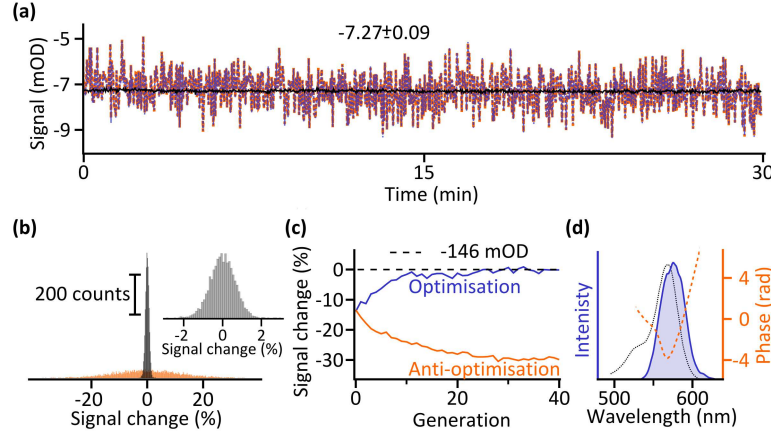


Figure 8.5: **Performance of the self-referenced experiment.** (a) Comparison of the signal magnitudes measured for E_{control} (blue, dotted) and $E_{\text{reference}}$ (orange, dotted) with the ratio of the two (black). The pump focus was adjusted to $82 \mu\text{m}^2$, the probe focus to $48 \mu\text{m}^2$. The signal error of CC_{target} is given at 95% confidence interval. (b) Histograms for CC_{target} (black) and $E_{\text{reference}}$ (orange). (c) Mean performance of each generation for a high field phase only CC experiment for both optimisation and anti-optimisation of the SE signal. (d) Optimum phase obtained for the minimisation experiment (orange, dashed) in comparison to the excitation pulse spectrum (blue) and the absorption spectrum of RHO101 dissolved in methanol (black, dashed).

act with a molecule and even linearly chirped pulses can drastically influence the efficiency of population transfer from the ground to the excited electronic state.^{239,260}

We used the same GA as Prokhorenko *et al.*²⁴⁶ based on the *Genetic Algorithm Toolbox* developed at the Department of Automatic Control and Systems Engineering of The University of Sheffield, UK. The shaping space is limited to phase only $(-2\pi, 2\pi)$ with a resolution of 6 bits. A total of 30 variables is used over the 530-610 nm shaping space which is linearly interpolated to cover the full shaping space on the SLM liquid crystals mask of 160 pixels. Initially, we generate a random guess to generate the zeroth population of 50 individuals. Each individual possesses a chromosome of $6 \cdot 30 = 180$ bits. After evaluating the performance, or fitness, as CC_{target} , measured as the SE signal in the 620-680 nm spectral range at a pump-probe delay of 30 ps, we select 50% of the individuals by stochastic undersampling based on their fitness values. The chromosomes of the "survivors" are used as a gene-pool for the second guess. We exchange bits between chromosomes (gene crossover at a 70% probability per chromosome) and randomly flip bits (mutation at a 60 % probability per

chromosome) to generate 25 new individuals. This first generation is evaluated as CC_{target} for either the maximisation (optimisation) or minimisation (anti-optimisation) of the signal of RHO101. This process is repeated until convergence is reached.

Figure 8.5c shows the results obtained for the high field optimisation and anti-optimisation experiments. Here, we normalised the signal level to CC_{target} for a TL excitation pulse. The initial population performs, on average, much worse than the TL pulse, which is expected in a high field scenario with a non saturated excitation transition. Here, many different pulse shapes can induce efficient stimulated emission from the excited back to the ground electronic state and hence decrease the SE signal and with it CC_{target} .^{260,261} In the optimisation experiment the signal recovers to its initial value whereas a 30% signal decrease is achieved in the anti-optimisation attempt. Importantly, the normalised signal level can not be optimised beyond the TL case in agreement with our expectations for high field CC. Evaluation of the anti-optimal phase obtained after GA convergence reveals a, in first approximation, linear chirp which is a well known pulse shape for efficiently decreasing the population transfer probability to an excited electronic state (Figure 8.5d).²³⁹

Weak field self-referenced coherent control

After verifying that a high enough signal stability can be achieved and that the GA is capable of optimising a trivial control target we will now test WF SRCC in a situation where no control should be possible. This experiment will allow us to identify possible artefact sources in measuring CC_{target} . Even though the stability measurements performed previously (8.5a,b) suggest high quality referencing of the signals generated by $E_{control}$ and $E_{reference}$ the situation is different if GA optimisation is performed. The GA does not distinguish between referencing artefacts and the CC target and will necessarily identify any experimental flaw by optimising towards it. In other words, compared to random signal fluctuations the GA is a much more difficult noise source to reference for as it actively searches for experimental weaknesses.

We introduce an 8 cm BK7 glass rod into the beam path of $E_{control}$. Now, $E_{reference}$ is identical to $E_{control}$ and it should therefore be impossible to induce changes in CC_{target} . To mimic possible experimental difficulties we slightly de-tune the phase matching angle in the fs-NOPA used for the generation of the pump pulse. This angle mismatch introduces some spatial chirp into the beam

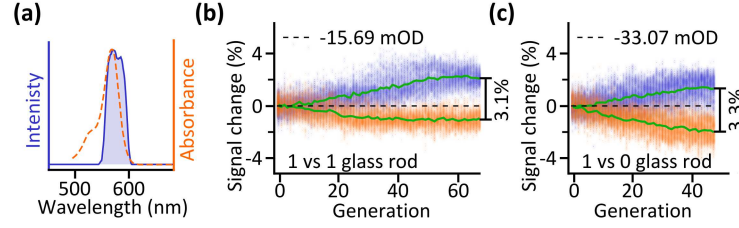


Figure 8.6: **Performance of the WF SRCC.** (a) Absorption spectrum of RHO101 dissolved in methanol (orange, dashed) at an $OD = 0.7$ in a $200 \mu\text{m}$ flow cell in comparison to the 23 fs excitation pulse spectrum (blue, solid). Pump and probe foci were adjusted to $78 \mu\text{m}^2$ and $46 \mu\text{m}^2$ respectively. (b) Optimisation (blue dots) and anti-optimisation (orange dots) for WF SRCC with two identical, chirped, pulses. The mean of each generation is shown in green. The pump power was adjusted to $\sim 12 \text{ nJ}$. (c) Fitness values for WF SRCC with an initially TL E_{control} pulse and a strongly chirped $E_{\text{reference}}$ field as: optimisation (blue dots) and anti-optimisation (orange dots). The mean performance of each generation is shown in green. The pump power was adjusted to $\sim 25 \text{ nJ}$. Result of 16 individually performed experiments are summarised in both figure (b) and (c).

as the signal wavevectors are no longer perfectly parallel during the amplification process. This spatial non-uniformity makes perfect alignment of the CC setup more challenging and hence artefact prone.

The WF optimisation and anti-optimisation experiments on the population transfer in RHO101 dissolved in methanol (15-33 mOD SE signal at a sample OD of 700 mOD) are performed with a 23 fs excitation pulse resonant with the blue part of the absorption spectrum (Figure 8.6a). 30 variables over the 540-610 nm spectral range, at 6 bit resolution, are used for both phase ($-2\pi, 2\pi$) and amplitude (0-1) shaping. The amplitude modulation induced change in excitation levels is accounted for within $\pm 5\%$ of the original SE signal by computationally scaling the amplitude mask. For evaluation we average the signal in the 620-680 nm SE region of RHO101 at a pump-probe delay of 30 ps and normalise to CC_{target} for an unshaped electric field. Contrary to Prokhorenko *et al.*²⁴⁶ we chose not to use the bleach signal for GA feedback as we found that even weak pump scattering can introduce CC artefacts.

Surprisingly, both the optimisation as well as the anti-optimisation experiments suggest successful WF CC even though E_{control} and $E_{\text{reference}}$ are nominally identical (Figure 8.6b). This observation, however, can be rationalised by considering the effect of a spatially non-uniform beam that renders a perfectly balanced alignment of the two experiments difficult. The total amount of con-

trol, computed as the difference between optimisation and anti-optimisation experiments, is, however, on the order of only 3%, lower than previously reported results for phase only CC of RHO101(6%)²⁴⁶ and the detection of the latter should thus be possible in an experiment with a non-chirped pulse.

The observation of a 3% shaping artefact highlights the difficulties associated with signal referencing in the presence of a GA. From our stability measurements (Figure 8.5a,b) we would have expected no control and, indeed, the same signal spread is observed in the initial generations of the SRCC experiment. The GA, however, identifies a referencing weakness and converges, suggesting that two identical electric fields can cause different amounts of population transfer. Importantly, these referencing difficulties are undetectable in stability measurements and only manifest themselves once a feedback guided search is performed. We note that the (anti)-optimal phase and amplitude masks differ between all experiments and it is therefore impossible to identify the presence of artefacts by reoccurring, and possibly trivial, pulse shapes.

After having identified the 3% artefact contribution to CC_{target} we are now in a position to perform WF SRCC. We remove the glass rod from the $E_{control}$ beam path and repeat the experiment with a slightly increased excitation level but at, otherwise identical conditions. Surprisingly, we observe results identical to those obtained in the previous experiment. The difference in CC_{target} between optimisation and anti-optimisation is on the order of 3% (Figure 8.6c). The differences between the absolute magnitudes of CC_{target} in the (anti)-optimisation experiments can be explained by slight changes caused by realignment of the beam path after removal of the BK7 rod.

This finding suggests that a strongly chirped pulse of ~ 1.5 ps duration performs equally well as a 23 fs pulse, or in other words that the phase of the electric field has no effect on the outcome of the WF CC experiment which leads us to conclude that all shaping artefacts must be due to amplitude modulation. Complete elimination of these artefacts should thus be possible by normalising the value of CC_{target} obtained for phase plus amplitude control to a second measurement where only the amplitude modulation is applied.

Broadband weak field self-referenced coherent control on rhodamine 101

One reason for the absence of WFPO control might be the limited bandwidth of the excitation pulse and hence the possibility to superimpose the required

vibrational energy levels. By increasing the bandwidth towards an 11.5 fs TL temporal electric field envelope, matched to the absorption spectrum of RHO101, we eliminate this limitation (Figure 8.7a). Additionally, we decrease the excitation level to ~ 10 mOD (pump power of 8.5 nJ), corresponding to excitation of only 1.5% of all molecules.

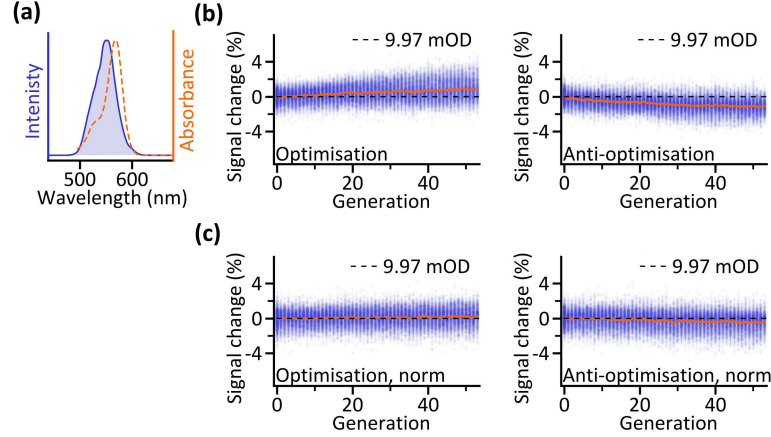


Figure 8.7: **Broadband WF SRCC of rhodamine 101.** (a) Absorption spectrum of RHO101 dissolved in methanol (orange, dashed) at an $OD = 0.7$ in a $200\ \mu\text{m}$ flow cell in comparison to the broadband, 11.5 fs, excitation pulse (blue, solid). Pump and probe foci were adjusted to $70 \times 75\ \mu\text{m}$ and $50\ \mu\text{m}^2$ respectively. (b) Results obtained for optimisation and anti-optimisation SRCC experiments on RHO101, without correcting for amplitude shaping induced artefacts. All the fitness values recorded in a total of 56 SRCC experiments (28 each) are included in the figure (blue dots), the mean value of each generation is indicated by the orange line. (c) As in (b) but with correction for amplitude shaping induced artefacts by normalisation of CC_{target} to a measurement performed with amplitude-only shaping.

The spectral shaping range is adjusted to 490-605 nm. Experiments with 32 and 50 phase and amplitude parameters, at 6 bit, are performed corresponding to spectral resolutions of 3.6 and 2.3 nm, respectively. Additionally, the phase shaping space is set to either $(-2\pi, 2\pi)$ or $(-4\pi, 4\pi)$ to eliminate possible limitations of the achievable pulse shape which might possibly be caused by imperfect phase wrapping. All other experimental parameters are kept as described previously.

The results obtained for both optimisation and anti-optimisation experiments, without correcting for amplitude shaping induced artefacts, are shown in Figure 8.7b. Signal changes on the order of $\pm 1\%$ are achieved and we conclude that no improvement in the amount of WFPO control could be achieved by matching the pulse bandwidth to the full extent of the RHO101 absorption

spectrum thus covering all possible vibronic transitions. To evaluate the actual amount of WFPO control we normalise CC_{target} for the amplitude shaping induced signal changes. The estimated maximum amount of WFPO control in RHO101 is smaller than $0.5\% = \pm 0.25\%$ (Figure 8.7c), much lower than the previously reported $+6\%$.²⁴⁶ We note that the amplitude induced artefact could be reduced to 2% by operating the NOPA under broadband phase matching conditions even though the pulse bandwidth, and hence the extend of spatial chirp, was increased. At bandwidths of ~ 100 nm it is, however, difficult to fully eliminate these spatial non-uniformity unless more complicated NOPA designs are introduced.²⁶²

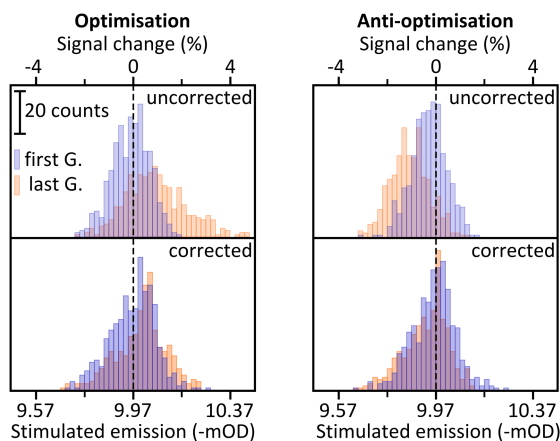


Figure 8.8: Histograms of the fitness values obtained for the first and the last generation during GA optimisation in the broadband WF SRCC experiments on RHO101. Data for both amplitude shaping artefact corrected and uncorrected experiments is shown.

We conclude with a comparison of the fitness distributions obtained for the SRCC experiments on RHO101 for the first and the last generation of the GA optimisation in both the corrected and the uncorrected experiment (Figure 8.8). Both the optimisation as well as the anti-optimisation attempts show a clear distribution shift if amplitude artefacts are not accounted for. Upon correction, however, the distributions merge and become almost indistinguishable.

Weak field coherent control on bacteriorhodopsin

The lack of WFPO CC pathways for the population transfer in RHO101 could be due to unfavourable dephasing, or dissipation. A different molecule might be better suited for WFPO CC. We chose bR, a highly reactive system with

CI mediated photoproduct formation with a 500 fs time constant. This reaction rate is faster than common vibrational dephasing times and a shaped wavepacket might exhibit considerable amounts of WFPO CC as underlined by the reports of $\pm 20\%$ phase plus amplitude and $\pm 6\%$ phase only control by Prokhorenko *et al.*²⁴⁵

We generate a 14.4 fs excitation pulse resonant with the absorption spectrum of bR (Figure 8.9a). As in previous experiments, bR (see Chapter 5)^a is suspended in MilliQ water at an OD of 0.49 in a 500 μm flow cell and kept in its light adapted form by means of a fluorescent lamp equipped with both UV and NIR filters. To ensure WF behavior we reduce the signal level measured at the maximum of the photoinduced absorption to ~ 2.3 mOD. $\text{CC}_{\text{target}}$ is computed from the differential photoproduct signal in the 620-700 nm spectral region at a pump-probe delay of 30 ps. A total of 66 shaping parameters (33 phase 33 amplitude) over the 520-620 nm shaping range are employed, resulting in a spectral resolution of 3.0 nm. Additionally, the size of the zeroth generation is reduced to 30 individuals and the shaping space set to $(-2\pi, 2\pi)$ for phase and $(0, 1)$ for the amplitude values. All other GA parameters are as previously defined.

Figure 8.9b shows the summarised results obtained for 20 CC experiments (10 optimisation, 10 anti-optimisation) performed on bR. As in the SRCC on RHO101 our data shows no evidence for WFPO CC which might be due to unfavourable dissipation parameters²⁵¹ but can not be attributed to insufficient signal stability for GA convergence which we measure to being 2.302 ± 0.048 mOD within a 95% confidence interval at 1 s integration time.

We change the dephasing environment by moving towards the retinal protonated Schiff base containing protein rho. Rho performs an 11-*cis* to all-trans RPSB isomerisation within ~ 200 fs with a quantum efficiency identical to that of bR (0.65). Additionally, the photoreaction proceeds three times faster and the negative effect of dissipation might be less pronounced, or even favourable.

The rho samples are isolated from bovine retinas and are dissolved in Ammonyx LO detergent^b at an OD of 0.45 in a 500 μm flow cell. Prior to the WF SRCC experiments we add hydroxylamine, at $2 \text{ mmol}\cdot\text{l}^{-1}$, to the solution in order to remove isomerised RPSB molecules from the protein pocket. Due to

^aThe bacteriorhodopsin sample was kindly provided by Dr. Garrick Taylor

^bThe rhodopsin samples were kindly provided by Dr. Katelyn Spillane

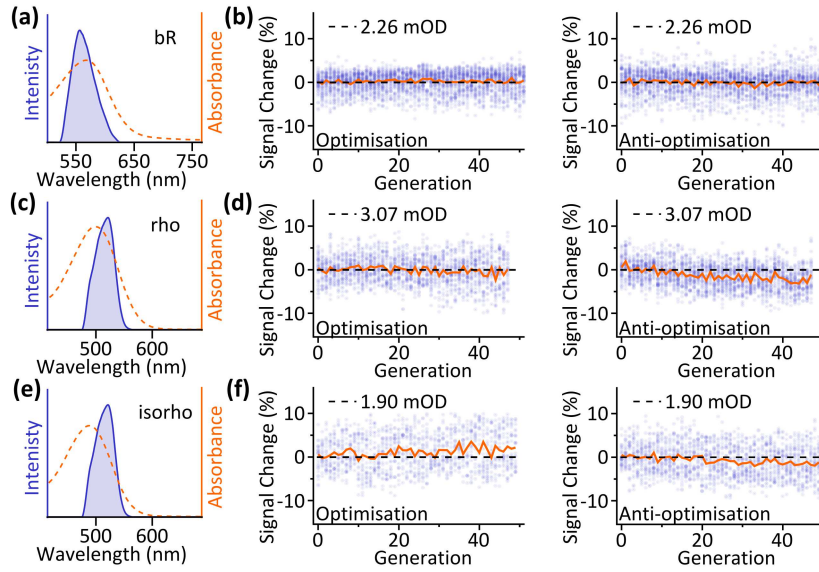


Figure 8.9: Weak field coherent control on retinal protonated Schiff base containing opsin proteins. (a) Spectrum of the 7.1 nJ excitation pulse (blue, solid) in comparison to the absorption spectrum of bR (orange, dashed). Pump and probe foci are adjusted to $63 \times 67 \mu\text{m}^2$ and $43 \mu\text{m}^2$, respectively. (b) Amplitude artefact normalised optimisation and anti-optimisation experiments performed on bR. Individual fitness values (blue dots) are shown in combination with the mean performance (orange line). (c) Spectrum of the 9.8 nJ excitation pulse (blue, solid) in comparison to the absorption spectrum of rhodopsin (rho) (orange, dashed). Pump and probe foci are adjusted to $61 \times 75 \mu\text{m}^2$ and $40 \mu\text{m}^2$, respectively. (d) As (b) but for rho. (e) Spectrum of the 17.2 nJ excitation pulse (blue, solid) in comparison to the absorption spectrum of isorhodopsin (isorho) (orange, dashed). Pump and probe foci are adjusted to $61 \times 75 \mu\text{m}^2$ and $40 \mu\text{m}^2$, respectively. (f) As (b) but for isorho. All experiments are performed at a laser repetition rate of 2 kHz in order to reduce protein damage caused by flow induced shear. Scattering induced signals of larger than $\pm 12\%$ in $\text{CC}_{\text{target}}$ are re-evaluated during GA performance. The integration time per pulse shape is increased from 100 ms to 1 s in order to account for the reduced signal-to-noise ratio due to both the five times lower repetition rate as well as the scattering.

the limited compression range of our chirped mirrors the excitation pulse spectrum is restricted to wavelength above 485 nm and the spectral overlap with the absorption spectrum of rho is therefore less ideal than in the experiment performed on bR. If we consider homogeneous broadening of the individual vibronic transitions, however, the pulse should be sufficiently resonant to generate vibrational wavepackets in all degrees of freedom contributing to the electronic transition. The signal magnitude at the maximum of the photoinduced absorption is adjusted to ~ 3.1 mOD and $\text{CC}_{\text{target}}$ is evaluated at a pump-probe delay

of 30 ps in the 585-635 nm spectral region. Rho photobleaches after isomerisation and we are therefore only able to perform a total of 10 CC experiments (5 optimisation, 5 anti-optimisation), results of which are shown in Figure 8.9d. Again, no evidence for photoproduct optimisation due to WFPO CC is found. Within the performance of the experiment we are, however, not able to firmly exclude the possibility of an anti-optimisation.

To conclude we move towards isorho dissolved in Ammonyx LO detergent at an OD of 0.37 in a 500 μm flow cell ^c. As the absorption spectra of rho and isorho differ only marginally from each other the same excitation pulse spectrum is used (Figure 8.9e). Analogous to rho, hydroxylamine at 2 mmol·l⁻¹, is added prior to the CC experiments to remove the isomerised RPSB chromophore from the protein pocket. We adjust the signal level to 1.9 mOD at the maximum of the transient photoproduct signal and leave all other experimental parameters as in the case of rho. The results obtained for a total of 6 CC experiments (3 maximisation, 3 minimisation) are shown in Figure 8.9f. Within the signal stabilities no evidence for WFPO CC is found.

8.3 Discussion

The results presented here are in contrast to previous observations on bR and RHO101 by Prokhorenko *et al.*^{245,246} but agree with the observation of no WFPO CC in bR by Florena *et al.*²⁶⁰ We developed a self-referenced CC approach that drastically facilitates CC in the WF limit. With our methodology, we measure the efficiency of a photoreaction with respect to a strongly chirped control pulse, rather than to a TL pulse. Even if the strongly chirped reference field could WFPO control a photoreaction it is highly unlikely that the amount of control would be identical to that of an unchirped electric field. The difference in performance between the two fields should result in a measurable difference and hence convergence of the feedback loop during an optimisation experiment. As we are unable to achieve any measurable control we conclude that WFPO CC is impossible, or very inefficient, in the four studied systems.

In retrospect the observations by Prokhorenko *et al.* are not surprising. It is well known that pulse-shapers operated in 4f configuration can induce severe spatio-temporal coupling.^{92,263–265} According to their experimental description no double pass, or 8f-setup, was employed to suppress such difficulties.

^cThe isorhodopsin samples were kindly provided by Dr. Katelyn Spillane

Even though very thorough intensity referencing was performed beam displacements and distortions cannot be accounted for by estimating the number of absorbed photons as the signal is a function of the shaping induced changes in the pump-probe overlap. As demonstrated in our experiment on RHO101, with two identical electric fields with slight spatial chirp, a GA is well suited for uncovering artefact sources. It is thus not surprising that the GA will synthesise electric fields that exploit, for example, beam distortions. Especially the anti-correlation of the optimal and anti-optimal pulse spectra as well as the equal amounts of optimisation and anti-optimisation efficiency obtained in bR hint towards such an artefact.²⁴⁵ Additionally, almost identical control results (20% amplitude plus phase, 6% phase only) were obtained for two distinctly different systems which suggests that most systems exhibit the same amount of controllability and hence very similar PES, or, that the same artefact source is present in both experiments.

Prokhorenko *et al.* rationalise their observation of amplitude shaping induced WF CC by a wavepacket generation mechanism that relies on correctly spaced spectral features. The generation of a 200 cm^{-1} vibrational wavepacket, for example, would require an accordingly modulated pulse spectrum.

To generate a vibrational wavepacket, by photoexcitation, we require two electric field interactions with the control field. These two interactions have to occur within the electronic dephasing time of the molecular system after which the fate of the photon has been decided hence it has either been scattered or absorbed. For bR the electronic dephasing time has been measured by Kennis *et al.* to being $\sim 50\text{ fs}$.²⁶⁶ Within this time scale our chirped referencing field, $E_{\text{reference}}$, possesses a bandwidth of only $\sim 50\text{ cm}^{-1}$. Given this limitation it is impossible to achieve an amplitude shaping governed control mechanism based on spectral spacings of 200 cm^{-1} as suggested by Prokhorenko *et al.*²⁶⁷ with $E_{\text{reference}}$. The SRCC approach should therefore be sensitive to both the WFPO as well as the amplitude control and hence converge to values of around 20% control. Given these considerations in combination with the complete absence of WFPO control in bR we conclude that the suggested CC mechanism outlined by Prokhorenko *et al.* is most likely not the reason behind the observation of an amplitude dependent photoproduct formation.

8.4 Conclusion and Outlook

Our observations raise the question whether WFPO CC is at all possible or not. The experiments suggest that the amount of control is much lower than previously thought but questions remain. In a system with favourable dissipation phase-only CC should be possible, the question is if such a system exists. Another problem for the implementation of WFPO CC are the electronic dephasing times which drastically limit the temporal shaping space. At room temperature, complex vibrational wavepackets would have to be generated within a time frame of 30-50 fs and ~ 10 fs pulses are most likely not short enough to achieve this target. Additionally, if low frequency modes are necessary for achieving efficient control than the electronic dephasing time might prohibit the generation of the ideal CC vibrational wavepacket.

The combination of ultrashort ~ 5 fs pulses with low temperature experiments, and hence longer electronic dephasing times, might ultimately be necessary to answer the question of whether weak field phase only coherent control is possible or not. At room temperature, however, the possibility to achieve such control seems unlikely.

Chapter 9

Summary and Outlook

9.1 Summary

The purpose of this work was to develop an ultrafast spectrometer, based on an Yb:KGW amplifier, that reliably records coherent vibrational oscillations at high spectroscopic $\sim 10^{-6}$ sensitivities.

Moving away from a Ti:Sapphire amplifier made it necessary to re-establish most of the readily available designs for optical instrumentation. The implementation of two non-collinear optical parametric amplifiers for the generation of sub-10 fs pulses in the visible and in the near infrared spectral range, pumped at either 343 or 515 nm, was a major step towards spectroscopic experiments (Chapter 3). Additionally, the identification of optimum whitelight continuum generation conditions allowed us to perform experiments at high levels of sensitivity without the need of probe referencing and thus drastically reduced the complexity of the experiments.

Spectroscopically, the key achievement was the observation, and isolation, of the pure S_1 vibrational coherence of β -carotene over the 100-1800 cm^{-1} spectral range by using broadband impulsive vibrational spectroscopy in combination with an automated subtraction algorithm (Chapter 4). The capability of being able to reliably record excited electronic state Raman spectra, in the time domain, allowed us to confidently assign the vibrational coherence observed in most of the follow up experiments to their respective electronic state of origin.

Having established a methodology to identify excited state vibrational coherence we attempted to answer the question of how wavepackets evolve after being generated in the Franck-Condon region of a reactive molecule (Chapter 5). We chose the historically well studied proton-pump bacteriorhodopsin

because of the spectrally well separated ground state absorption and stimulated emission transitions and the fast isomerisation rate. The isomerisation proceeds faster than vibrational dephasing and vibrational coherence might therefore influence the reaction. We identified vibrational coherence after photoexcitation, but no evidence for the dynamical frequency changes during the coherence evolution on the excited electronic state could be found. The major finding of this work was that even though the vibrational coherence generated by excitation into the Franck-Condon region is known from resonance Raman intensity analysis anharmonic coupling on the excited electronic state seems to rapidly transfer the initial coherence activity to different vibrational modes. This transfer must be fast as we find no evidence for shifting frequencies but cannot be instantaneous as no ground state resonance Raman activity is present for many of the detected, S_1 active, modes.

We addressed the question of how vibrational coherence is effected by electronic surface crossings by performing experiments on β -carotene (Chapter 6) as a model system. After vibrational coherence generation in the second excited electronic state by photoexcitation we followed the wavepacket evolution into the first excited state. Wavepacket activity in all S_1 modes, after electronic surface crossing, showed that internal conversion through a conical intersection proceeds in a vibrationally coherent fashion. Additionally, strong activity in non-totally symmetric modes was observed, suggesting that the photoexcited system is oscillating in the vicinity of the conical intersection where the S_2 and S_1 potentials are strongly vibronically coupled. Even though the internal conversion time from S_2 into S_1 is around 140 fs we did not observe the expected rise of the S_1 vibrational coherence. S_1 wavepacket activity is already present at time zero suggesting that a vibronic superposition of S_2 and S_1 is initially excited.

In both the bacteriorhodopsin as well as the β -carotene project (Chapters 5 and 6) we employed electronic population control for the identification of excited state vibrational coherence. By combining these projects with the excited state Raman work on β -carotene (Chapter 4) we developed a technique that enabled us to experimentally isolate baseline free excited state Raman spectra, without any solvent or ground state contaminations (Chapter 7). After generation of vibrational coherence on an excited electronic state we partially deplete its population with a so-called "dump" pulse. Modulation of the dump pulse

directly isolates the pure excited state signal and Raman spectra of comparable, or better, quality than femtosecond stimulated Raman spectroscopy are obtained.

Additionally, we performed weak field quantum coherent control experiments on a variety of systems: Rhodamine101, rhodopsin, isorhodopsin and bacteriorhodopsin (Chapter 8). Initially, these experiments proved prohibitively difficult due to problems associated with artefacts suggestive of successful coherent control. After developing a signal referencing technique based on a strongly chirped reference pump and elimination of beam displacements during pulse shaping by implementing an 8f-grating stretcher design we found, in contrast to previous works, that no coherent phase only control ($<1\%$) can be achieved in the one-photon limit.

9.2 Outlook

Ytterbium based fs-fiber lasers²⁶⁸ are emerging as powerful, stable and relatively simple alternatives to Ti:Sapphire amplifiers. I hope that my ground work on ultrafast spectroscopy and optical instrumentation for 1030 nm systems will be helpful for the future development for more advanced spectroscopic techniques and experiments.

Many of the experiments presented in this work were "first-time" proof-of-principle experiments such as: the first excited state Raman spectrum recorded over the full vibrational manifold in the time domain, the first observation of vibrational coherence in an excited electronic state generated by the photoexcitation pulse (beyond low frequency modes $<500\text{ cm}^{-1}$) and the first observation of a vibrationally coherent internal conversion process. This work established vibrational coherence as a possible probe for excited state dynamics and the, otherwise, hard to access event of electronic surface crossings. To ultimately unravel the structure of conical intersections we started to work on a variety of systems such as rhodopsin, pentacene thin films,²⁶⁹ carotenoid aggregates^{270,271} and myoglobin.¹⁵ I hope that our results will help to broaden the understanding of ultrafast conversion processes and will motivated other groups to perform similar experiments.

Time resolved excited state Raman spectra recorded in the time domain should allow us to access the very early time scales of molecular evolution out of the Franck-Condon region. Here, frequency domain Raman techniques suffer

especially from nonlinear signal contributions which can be removed in time domain measurements. Even though the nominal temporal resolution of any ultrafast Raman experiment is limited by the vibrational dephasing times an ultrashort impulsive pulse should allow us to imprint the mode specific displacements within the Franck-Condon region into the subsequently recorded vibrational coherence. By doing so we should be able to directly map the structure of the potential energy surface in the Franck-Condon region. Our experiments on bacteriorhodopsin suggest that most of the anharmonic coherence activation takes place during the evolution out of the Franck-Condon region and mapping the precise potential structure should give valuable insights into the factors governing the coupling process.

Many open questions remain such as the precise factors governing the wavelength dependent vibrational coherence activity observed in our Fourier intensity maps such as the position of mode specific phase jumps. Can a better understanding of these intensity distributions allow us to extract information on the precise position of vibronic transitions composing an absorption spectrum? Experiments on systems with internal conversion times of ~ 300 -400 fs would be interesting. Here, the exact frequency content of the vibrational coherence activity in both the initial as well as the final electronic state should be observable. Knowledge of these activities, and how they differ, will allow for the identification of the explicit coordinates spanning a conical intersection. For collaborative theoretical-experimental work the generation of ~ 10 fs pulses in the 200-300 nm spectral range is necessary. Even though such experiments will be very challenging they would greatly benefit our understanding of the principles behind the breakdown of the Born-Oppenheimer approximation. Despite the difficulties associated with cascading signals in 2D-Raman spectroscopy^{272,273} the time domain approach allows for the unique possibility to directly measure the anharmonic coupling present in the strongly distorted Franck-Condon region. By generating ground electronic state vibrational wavepackets and then photo exciting the system with a second, fully resonant, pulse it should be possible to directly extract which Franck-Condon active modes contribute to the vibrational coherence transfer by looking at the off-diagonal bands of the 5th order response function.

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