

**SPONTANEOUS TRANSIENT ULTRAFAST COHERENT RAMAN
SPECTROSCOPY**

by

Seth Meiselman

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics

Spring 2016

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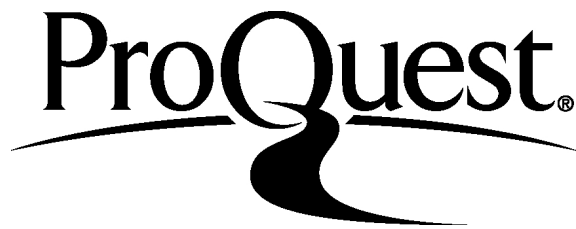
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by

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There's always someone missing from a list like this. But that's just the way things go. If you've been left out here, please know it wasn't on purpose. Maybe I should have kept this saying "This page intentionally left blank."

My family has been highly supportive of this dissertation process. I can't remember how many times I got a phone call from my dad who started the conversation with "Have you written anything yet?" The constant nudging, while in the moment could become an annoyance as every other person who has undergone this process must know, felt like a lifeboat at times. And especially now, I can finally answer to you when I might be finished with my degree.

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To the entire department staff, in particular Deb and Maura, your help and patience was crucial to my success. Then there are the oddballs, past grad students like Tulasi or Laura, that know when to lend a deferent word or light-hearted jab. My frenemy, and roommate- Brian, for all the back and forth, the ups and downs, and downs, and other downs. You've been like a brother at arms, even outside playing hours and hours of Call of Duty or Borderlands games. Whatever the question, the answer will always be "yes".

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Gina...

When I started back in the Fall of 2009 a new assistant professor was setting up her lab space in the basement of UD's Sharp Lab. It wasn't until a month into my first term when she gave a seminar lecture to the new graduate students about her research that I found this out.

Hold up. Let's rewind a bit.

During my undergrad at Drexel University, I had a great experience with Dr. Tony Abi-Salloum at Widener University studying a light-matter phenomena. We were working on the theory and computational side of things, and had collaborators elsewhere. It was truly wonderful. And at his urge, I applied to graduate schools in hopes of continuing that type of investigation. I even applied to the wrong school. He had colleagues at Delaware State... but I had friends at UD. A miscommunication happened. I got accepted to UD, and in turn accepted that opportunity, but I had looked at the faculty in UD's Physics and Astronomy department when I got the letter, the website wasn't updated, and I didn't have a specific person in mind to work with- nothing piqued my interest - yet.

Ok, back to the story.

So there I was, green as can be, knocking on a new professor's door in early October of 2009 just a few days after she had given us a basic outline of her research plans.

“Yes, come in ...”

From that polite invitation I got something out of my graduate experience not many can claim. I don't know where to begin, Gina, you've challenged me at every step along the way, thank you. Thank you for letting me help you set up your lab. All the manual labor that went into it was the perfect start to experimentation. Thank you for asking me to take the lab apart. Shock and awe aside, I'm so excited for you and the group to succeed in Illinois I hope the dismantling process helped the others understand the work that went into the setup process. Thank you for asking me time and time again if I'd like to work on various projects. It's easy for me to get tunnel vision regarding research and literature reading. Thank you for the journal reports. Thank you for preventing me from getting complacent with what I know. Thank you for your example. Thank you for the arguments, the praise, and the occasional glare. Thank you for introducing me to the world of lab snacks! Thank you, from the bottom of my heart, for allowing me the privilege of being your first graduate student. I'm honored and humbled by the past seven years. I hope I wasn't too much of a hassle. :D Cheers!

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ABSTRACT

I explore the application of Transient Coherent Ultrafast Phonon Spectroscopy (TCUPS) to the measurement of vibrational coherence dynamics of liquid alcohols. The demonstrated technique is complementary to and, in some cases, simpler than traditional stimulated spectroscopy techniques in that it does not require more than one laser and is free of non-resonant background.

I demonstrate coherence measurements of single-photon-level collective excitations: a single vibrational state at 1033 cm^{-1} in methanol; a pair of simultaneous excited vibrational states at 2834 and 2944 cm^{-1} in methanol; and three simultaneous excited states at 2885 , ~ 2930 , and 2976 cm^{-1} in isopropanol. I develop a Fourier-transform-based analysis of the TCUPS data that overcomes poor signal-to-noise ratio and signal degradation due to etaloning and fluorescence. The coherence lifetimes and oscillation frequencies agree with frequency-domain line-shape measurements and femtosecond Coherent anti-Stokes Raman Scattering (CARS) measurements.

Chapter 1

INTRODUCTION

1.1 Raman Scattering

Inelastic scattering of light from a medium is commonly referred to, as a result of historical convention, as Raman scattering. This is because C.V. Raman and his group published widely viewed work in the latter half of the 1920's [1], while the effect predicted by Adolf Smekal a few years prior [2] was not well known, and the independently reported studies by Grigory Landsberg and Leonid Mandelstam [3] in what had amounted to the timing difference of the span of a single week had not yet spread to European researchers. Countless experimental and theoretical works have been performed since then, with reviews, progress reports and some textbooks being written in recent years.

In a scattering process, photons create an oscillating polarization as they pass into a medium and have a chance to couple to the native polarizations of the medium. If the polarizations do not couple, then the medium's state remains unaffected and the scattered photon's energy will stay the same. This is called elastic or Rayleigh scattering. If, however, the polarizations do couple, the medium may change by increasing or decreasing its energy state and as a result, the scattered photon has a corresponding decrease or increase of energy from that of the incident photon. The medium's energy states can be electronic, vibrational or rotational in nature. Our focus will be on this inelastic, Raman scattering of photons as it is often used to study vibrational modes [4, 5].

In our experiment, the Raman scattering makes use of the vibrational states within a molecule to shift the frequency of an incoming photon. The frequency of the

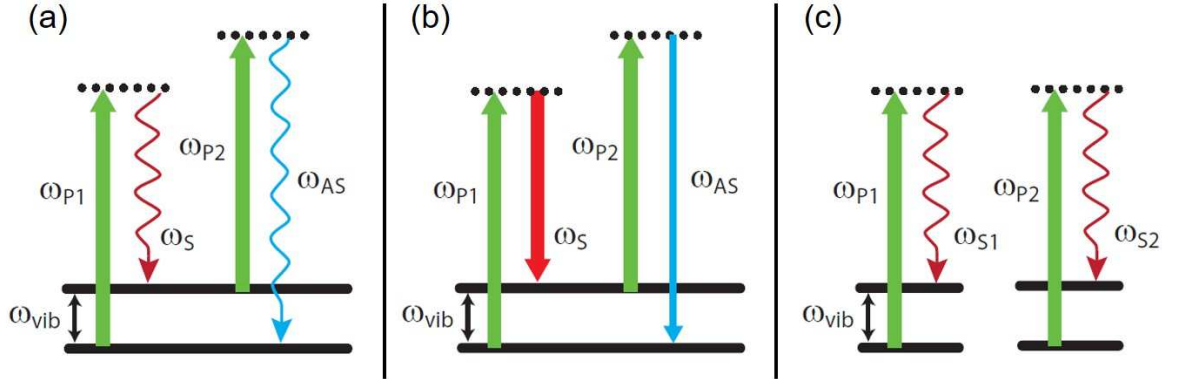


Figure 1.1: Raman scattering diagrams. ω_{vib} is representative of a vibrational energy difference between the lower ground state and the upper excited state. The dashed line represents a virtual state. (a) General Raman scattering of Stokes and anti-Stokes from two independent pumps. (b) CARS scheme; ω_{P1} , ω_{P2} , and ω_S are the first, second, and stimulating Stokes pumps respectively, yielding ω_{AS} , the stimulated anti-Stokes signal. (c) TCUPS scheme; here ω_{P1} and ω_{P2} act independently, spontaneously creating ω_{S1} and ω_{S2} .

scattered photon is $\omega_P \pm \omega_{vib}$, where ω_P is the incident photon frequency and ω_{vib} is the frequency of a molecular vibrational state, see Fig. 1.1.a. A negative frequency shift is associated with the excitation of a single vibrational state and the emission of a photon of frequency $\omega_S = \omega_P - \omega_{vib}$, called a Stokes photon – named after George Stokes for his work describing the phenomenon of fluorescence – and a positive frequency shift represents de-excitation, the removal of vibrational energy and the emission of an anti-Stokes photon of frequency $\omega_S = \omega_P + \omega_{vib}$. Since the vibrational modes of molecules are bond-specific, it is possible to retrieve a vibrational spectrum that is unique to the particular molecular system. Observation of isolated and cluster molecules [6], liquid-air interfaces [7], even environmental effects, in particular the impact of hydrogen bonding [8, 9, 10, 11] in solution [12, 13, 14, 15] have been reported. However it should be mentioned that Raman techniques alone are insufficient to gain all of the available information in every system, IR spectroscopy, x-ray, and neutron scattering techniques would also need to be utilized.

In recent decades much advancement has taken place in Raman scattering techniques: angular dependence [16]; vibrational dynamics through use of pico-second laser pulses [17]; stimulated Raman scattering [18]; multi-dimensional correlation spectroscopy [19, 20]; the effects of chirped pulses on stimulated Raman scattering [21]; the application and use of liquid-core waveguides [22, 23, 24]. A significant advancement came in the form of coherent anti-Stokes Raman scattering (CARS), see Fig. 1.1.b. CARS has many forms that work in both the frequency and time domain. In the basic interaction of CARS, a laser at the Stokes wavelength ω_S , represented by the red arrow in Fig. 1.1, stimulates the transition with the first pump field to the excited state. The second pump field ω_{P2} converts the material excitation into a polarization that radiates as the anti-Stokes photon.

For comparisons later, we will focus on transient CARS techniques. In transient CARS, the three fields are pulses in time, with variable time delays between the arrival of the individual pulses, see [12]. Like most techniques, CARS has some drawbacks, such as non-resonant background [25], and requires a laser at the Stokes wavelength whose bandwidth determines the range of energies over which excitations are simultaneously probed [26]. Still, the resolving power and high signal to noise make CARS a powerful technique for studying molecular systems [27, 28, 29, 30, 31, 32, 33, 34].

1.2 Transient Coherent Ultrafast Phonon Scattering

Waldermann *et al.* reported the Transient Coherent Ultrafast Phonon Scattering (TCUPS) technique in 2008 [35]. This technique allows investigation of the coherence dynamics of optical phonon modes in solid state systems using spontaneous Stokes generation. A pulsed pump beam's intensity is split by an interferometer and recombined with one of the two beams delayed in time with respect to the other. As the two pump pulses are derived from the same source, they have the same carrier-envelope phase. These delayed pulses are focused into a sample, in their case diamond, and each converting into an excitation pair of the phonon mode and emitted Stokes photon, see Fig. 1.2.

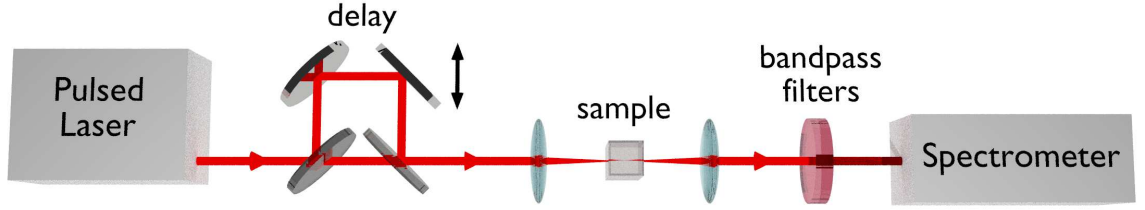


Figure 1.2: Simplified TCUPS setup.

In a semiclassical, frequency-domain picture, the incident pump pulses, delayed by τ , exhibit spectral fringes with a periodicity of $1/\tau$. The resultant Stokes light is measured and spectrally resolved with a slow detector. The Stokes light will also exhibit fringes, but as the delay τ increases the visibility will be reduced due to the linewidth of the Stokes light, which is a result of the finite lifetime of the coherence. For the case of diamond, the coherence lifetime may be limited due to crystal anharmonicity and impurities. The fringe visibility as a function of the delay between the pump pulses then represents the coherence dynamics.

We can alternatively interpret the TCUPS signal as a quantum mechanical Young's double-slit experiment, see Fig. 1.1.c, under the condition that less than one Stokes photon is created by each pulse. In this low population excitation limit, the first pulse has a chance to create an excitation pair of a Stokes photon and an optical phonon. This can be viewed as the first of two pathways or slits. Then, when the second pulse arrives, it too has a chance to create an excitation pair and this represents the second pathway. The measured emitted light is the sum of these two pathways, and like in Young's double-slit experiment if the two pathways are phase coherent the result is spectral fringes. As the time delay between the two pump pulses is increased, due to the finite lifetime of the excitation and thus finite coherence time of the Stokes photons, 'which-way' information becomes available about whether the first or second pulse created the excitation pair. This gain of information causes a decrease in the

visibility of the interference fringes.

To measure the coherence lifetime of the vibration, the pump pulse is in the transient regime where the duration of the pulse is faster than the decay of the coherence, yet slower than the phonon vibration frequency. TCUPS relies on spontaneous Stokes generation; this is in contrast to CARS, which stimulates the transition from the ground to excited state. As a consequence, TCUPS results in low population excitation numbers, which can be useful for avoiding excitation-induced broadening, such as hot phonons in diamond [35]. So TCUPS enables measurement of coherence dynamics at the single-excitation level.

In this thesis we extend the TCUPS scheme to study the coherence dynamics of single and multiple simultaneously excited vibrational modes in molecular liquids. In the process, we develop analysis techniques to overcome limitations due to poor signal-to-noise ratio.

1.3 Simple Alcohols

Extending TCUPS to the study of liquids presents a small dilemma: what material should we use? To answer this we looked through tables and resource texts searching for a suitable testing material [36, 37, 38, 39, 40, 41, 42]; our answer came in the form of simple alcohols, which are plentiful, common, and easy to handle. The simplest of all, methanol, is ubiquitous to the optics lab environment. Methanol gets used for everything from a cleaning agent to a dilute solution to study hydrogen bonding dynamics [43, 44]. So we use methanol as a benchmark because it is so well studied [45, 46, 47, 48, 49, 50, 51] and because it is an interesting case for the TCUPS scheme [52, 53]. Methanol has a very strong Raman shift at about 1033 cm^{-1} which would provide an excellent case study of a single vibrational mode.

Even in recent years, methanol has still had new information and characterization come out of it; for example, Yu *et al.* re-examined the Raman spectrum assignment of the simplest alcohol [54]. There are other materials for consideration as well. In fact, the whole group of hydrocarbon alcohols provides useful connections to biological

studies, and contain a variety of vibrational modes that have been well studied over the years [55, 56, 57, 58, 59, 60, 61, 62]. Applying TCUPS to such systems will allow us to reproduce previous reports and measure novel properties of vibrational systems.

Along with the strong Raman peak at 1033 cm^{-1} , methanol also contains two peaks of comparable amplitude in the C-H region around 2900 cm^{-1} . This two peak system would be a good test for TCUPS on multiple modes. Exciting multiple modes results in coherence oscillations, a phenomenon that has been observed in methanol, ethanol, etc. [12, 63]. We can study coherence oscillations due to simultaneous excitation of more than just two modes; there is not as much literature on such dynamics. Isopropanol (2-propanol), has more than two modes in its C-H region [64, 65], and we choose this system to test the applicability of TCUPS to many modes.

1.4 Walkthrough

With those motivations in mind, we now set out to show some of the TCUPS scheme’s capabilities. In Chapter 2 we present our experimental setup to measure vibrational state coherence lifetimes [66]. We then describe the theory behind the adopted TCUPS scheme [35] and an analogous CARS scheme. We extend the description to a system that exhibits coherence oscillations. Lastly we discuss some expectations from applying TCUPS to multiple mode systems based on numerical simulations.

In Chapter 3 we apply TCUPS to the simple alcohols: methanol and 2-propanol to study the scheme as it measures a one, two, or three simultaneously excited modes [66, 67, 68]. We describe a Fourier analysis procedure that we developed to address signal-to-noise degradation from various sources.

And finally, in Chapter 4 we conclude with a discussion of our findings and prospects for future work.

Chapter 2

EXPERIMENT

2.1 The Setup

A simplified schematic of the setup for the TCUPS experiment is shown in Figure 2.1, and a more detailed version is shown in Figure 2.2. We start with a Millennia Prime Nd:YAG diode laser which pumps a Tsunami Ti:Sapphire oscillator, both by Spectra-Physics. The lasing system induces a fixed-phase relationship between longitudinal modes in the cavity, ‘mode-locking’ itself. The interference between the modes causes the light to be produced in a train of pulses. The pulsing beam in this case has a repetition rate of 80 MHz, pulse duration of ~ 150 fs, and is centered in the region of 770 – 790 nm. The pulse bandwidth is approximately 12 nm, which is broad enough to observe spectral fringes for the TCUPS experiment. However, we still require the pulse duration to be short enough in time that we are slower than the decay of the coherence we wish to measure. So the transient regime required for TCUPS is satisfied by the mode-locked pulses.

The output of the Tsunami passes through a cylindrical lens pair for adjustment, to ensure a more symmetric transverse spatial profile. The beam then goes through a half wave-plate to rotate the polarization, then reflects through a polarizing beam splitter cube for adjusting the total power of the pump beam into the setup (and for allowing shared use of the beam). The pulsed pump beam is now s-polarized for the rest of the experimental setup.

The Raman signal at the focus of this work comes from the vibrational modes of liquid molecules and is much smaller than the wing amplitude of the pump. To help with the signal acquisition the pump then passes through a series of interference

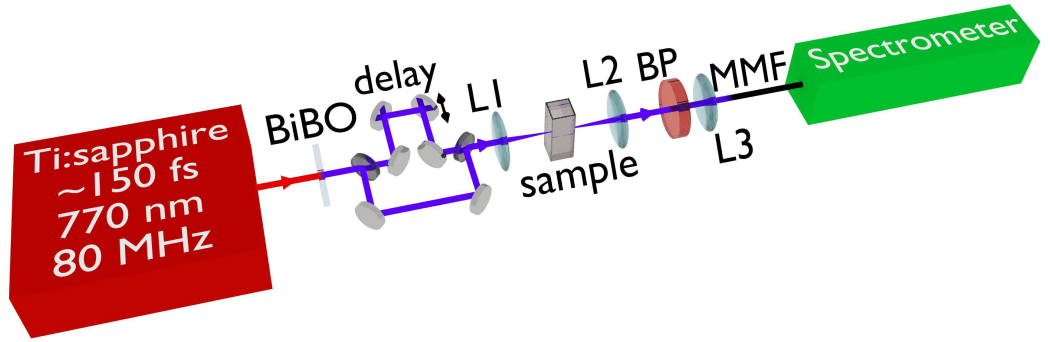


Figure 2.1: Simplified schematic showing the necessary components of the transient ultrafast coherent scattering experiment. BiBO, bismuth triborate second-harmonic generation crystal; L1-3, lens; BP, bandpass filter; MMF, multi-mode fiber.

filters to trim the amplitudes of the wings (see Fig. A.3.b, Table A.1). At this point the pump is focused using a pair of 50 mm spherical lenses into a bismuth triborate (BiBO) second harmonic generation (SHG) crystal. We had previously tested potassium titanyl phosphate (KTP) and β -barium borate (BBO) for other purposes and found BiBO better matched our needs for this and related work. The crystal is phase-matched for maximum frequency doubling in some instances of data collection; however, using the crystal slightly off phase-matching provides an extra means of control for the SHG output power in testing and for related work. The fundamental is then filtered from the SHG light by a notch filter, and a combination of band pass (or low pass) filters, (see Fig. A.3.e, Fig. A.1.a-c). The clean pump beam is then put through a Mach-Zender interferometer that uses two UV fused silica 50/50 beam-splitters coated for 400 – 700 nm from Thorlabs.

The interferometer provides an adjustable temporal delay between the two pump beams; for practical identification purposes the two arms will be addressed as fixed and delayed. The fixed arm has a half wave-plate that was adjusted to achieve equal power in both arms. The delay stage in the delayed arm is a Newport UTS50CC linear screw stage, operated through the Newport ESP301 Motion Controller. The colinear beams are then focused through a 25 mm focal length lens into a centimeter-deep standard

glass fluorometer cuvette that holds the liquid sample.

The pump and signal output is re-collimated by another 25 mm focal length lens. Before collection the signal is separated from the pump via a stack of four interference filters (see Fig. A.1.f). For diagnostic purposes and pump collection a stack of neutral density filters equating to ND-8 (or more depending on the current average power) was used. The light is collected by a M31L01 multimode fiber optic cable from Thorlabs. The fiber connects to an Andor Shamrock spectrometer (SR-303i-A) that used a 1200 lines/mm grating the photons are detected by an Andor iDus (420 Series) CCD camera, under most default settings and electronic cooling to -70°C .

For most of the data presented in this thesis the spectrometer had an acquisition time of two seconds for both signal and background spectra. Longer times had been observed, and shorter times attempted; however, this two second window seemed to provide the best signal-to-noise ratio given the instability of the interferometer.

Two methods were used for taking background spectra. The first method was using a far time (~ 800 ps) delay for which the interference is averaged out by the limited resolution of the spectrometer and CCD camera. The second is by blocking either arm of the interferometer and then numerically doubling the intensity of the unblocked arm's spectral counts. Both methods yield similar results and were utilized based on availability of required apparatus and experimental setup design for other work.

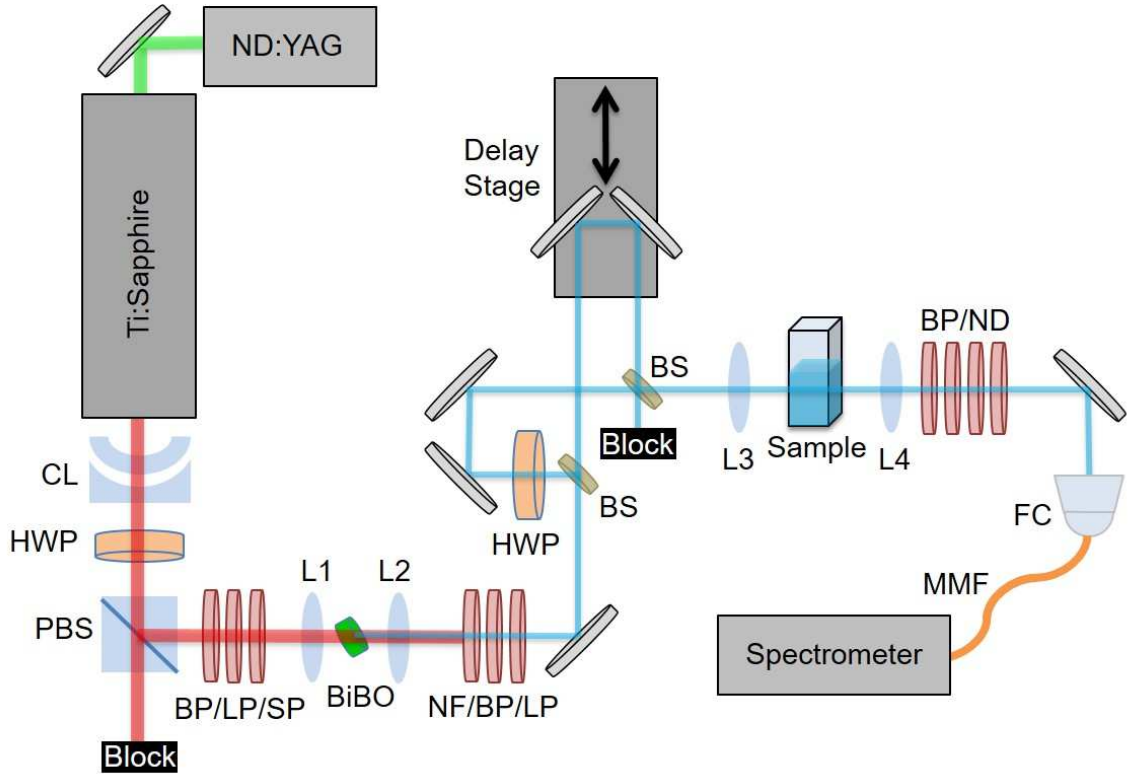


Figure 2.2: Complete schematic showing the components of the TCUPS experiment. CL, cylindrical lens pair; L1-4, lens; HWP, half wave plate; PBS, polarizing beam splitter; BS, 50/50 beam splitter; BP/LP/SP/NF/ND, band pass, long pass, short pass, notch, and neutral density filters; BiBO, bis-muth triborate second-harmonic generation crystal; FC, fiber coupler; MMF, multi-mode fiber.

2.1.1 Single-photon level

By working in the spontaneous regime, the TCUPS technique results in low population excitations and as such can be performed at the single-photon level. The following calculation is used to show the TCUPS technique used in this thesis is within the single-photon limit.

The rate of incident photons corresponding to an average pump power of 7 mW at 371 nm and a repetition rate of 80 MHz is

$$\sim 3.75 \times 10^7 \frac{\text{photons}}{\text{s} \cdot \text{pulse}}. \quad (2.1)$$

The focal area A of the beam through the 2.5 cm lens is $\sim 10^{-4} \text{ cm}^2$, with a Rayleigh length $L \sim 0.5 \text{ cm}$. The density of methanol is taken to be $\rho = 0.7918 \text{ g/mL}$; then the total mass of methanol inside the focal volume is $A \times L \times \rho \sim 4 \times 10^{-5} \text{ g}$. Using the molecular weight of methanol as $\sim 32 \text{ g/mol}$ yields approximately $1.25 \times 10^{-6} \text{ mol}$ or $N \sim 7.5 \times 10^{17}$ molecules.

The Raman cross section is $\sim 8.3 \times 10^{-30}$ for the 2830 and 2940 cm^{-1} modes in methanol [58], giving a total cross section of $\sigma \sim 16.6 \times 10^{-30}$. The 2.5 cm focal length with a collimated beam diameter of 7 mm gives a planar angle $\theta \sim 7^\circ$ corresponding to a solid angle $\Omega \sim 0.1 \text{ SR}$. Then the conversion factor for converting incoming pump photons to Stokes or anti-Stokes output photons is

$$\frac{\Omega N \sigma}{A} \sim 1.25 \times 10^{-8}. \quad (2.2)$$

Thus, with the incoming pump photon flux as $3.75 \times 10^7 \text{ photons/s}$, we find

$$\sim 0.5 \times 10^0 \text{ Stokes photons per pulse}, \quad (2.3)$$

$$\sim 6 \times 10^{-9} \text{ anti-Stokes photons per pulse}. \quad (2.4)$$

These output numbers do not include losses such as reflections ($\sim 5\%$), coupling to multimode fiber ($\leq 0.35 \text{ dB}$, see www.thorlabs.com), or spectrometer and camera detection efficiencies ($\sim 30\%$, see www.andor.com). From this calculation we find that we are within the single-photon limit for our detection, and that the probability

of measuring an anti-Stokes photon generated through a second order interaction is negligible. Likewise detecting two photons due to a single pulse exciting two molecules and creating a pair of Stokes photons also has a low probability of occurrence.

It is also worthy to note that the Boltzman factor $k_B T \sim 200 \text{ cm}^{-1}$ is less than the minimum vibrational Stokes shift (1033 cm^{-1} in methanol) studied in this TCUPS experiment, so thermal excitations are also neglected here.

2.2 TCUPS Formalism

2.2.1 Semi-classical derivation

We calculate the signal as a convolution of the frequency-domain laser spectrum $I_L(\omega, \tau)$ with the frequency-domain Raman gain $R(\omega)$ [26]. The incident laser field in the time domain is given by

$$E_L(t, \tau) = \frac{1}{2} (E(t)e^{-i\omega_L t} + E(t - \tau)e^{-i\omega_L(t - \tau)}) + c.c. \quad (2.5)$$

where $E(t)$ is the field envelope, ω_L is the laser center frequency, and τ is the delay between the pulses, see Fig. 2.3.a for the real part of the field in time. By applying a Fourier transform, in the frequency domain this is

$$E_L(\omega, \tau) = E(\omega - \omega_L)(1 + e^{i\omega\tau}) \quad (2.6)$$

where $E(\omega)$ is the field envelope centered at $\omega = 0$, and $E(\omega) = E^*(-\omega)$, with ω ranging over all frequencies, both positive and negative, see Fig. 2.3.b. The spectral intensity is

$$\begin{aligned} I_L(\omega, \tau) &= E_L^*(\omega, \tau)E_L(\omega, \tau) \\ &= E^*(\omega - \omega_L)(1 + e^{-i\omega\tau})E(\omega - \omega_L)(1 + e^{i\omega\tau}) \\ &= |E(\omega - \omega_L)|^2 [(1 + e^{-i\omega\tau})(1 + e^{i\omega\tau})] \\ &= I(\omega - \omega_L)(1 + e^{i\omega\tau}) + c.c. \end{aligned} \quad (2.7)$$

where $I(\omega - \omega_L)$ is the absolute square of the field envelope centered at ω_L . Since $I_L(\omega, \tau) = I_L(-\omega, \tau)$, we need only to consider positive frequencies.

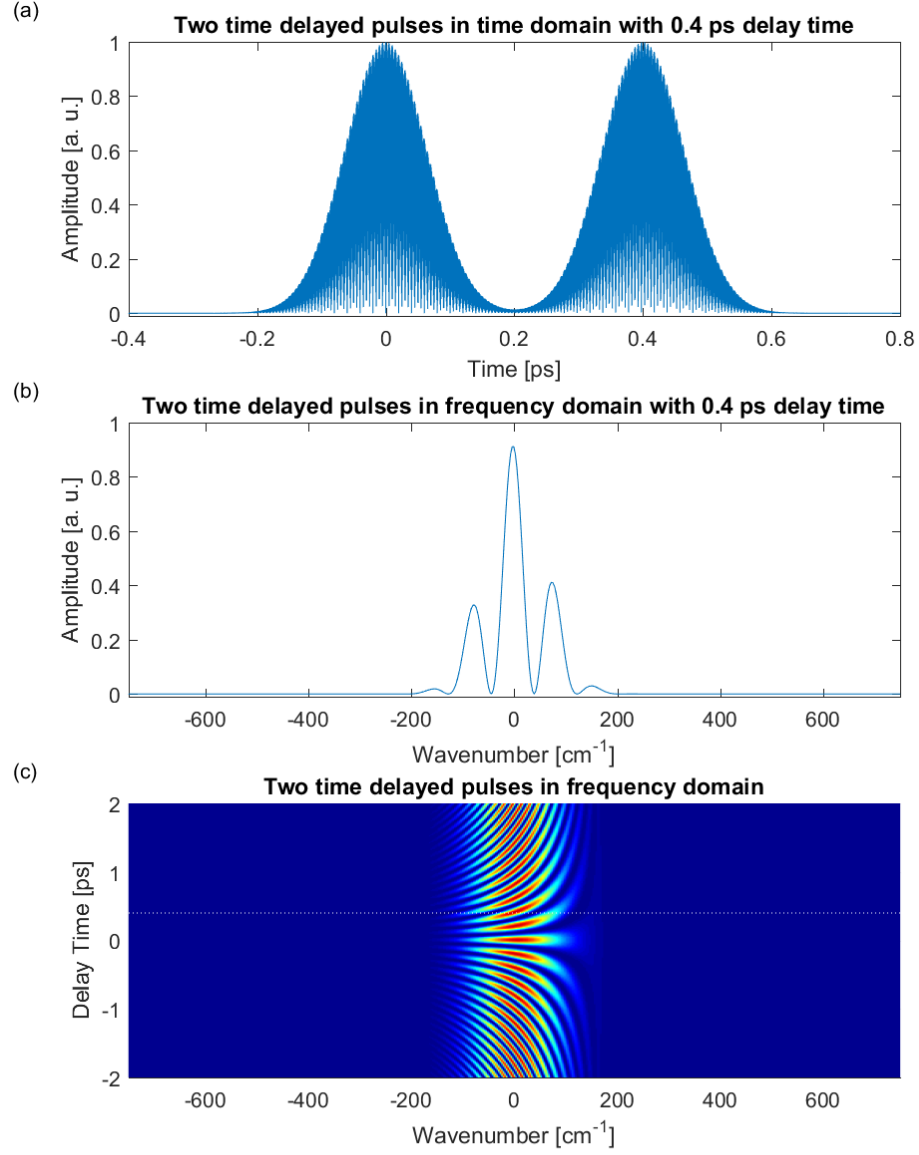


Figure 2.3: Simulated delayed pump pulses. (a) Two pump pulses in time; one centered at $t = 0$, the other centered at a $\tau = 0.4$ ps delay. (b) Two pump pulses delayed by $\tau = 0.4$ ps, in the frequency domain. (c) Various time delays for the two pump pulses, in the frequency domain. Dashed line corresponds to the $\tau = 0.4$ ps delay in (b).

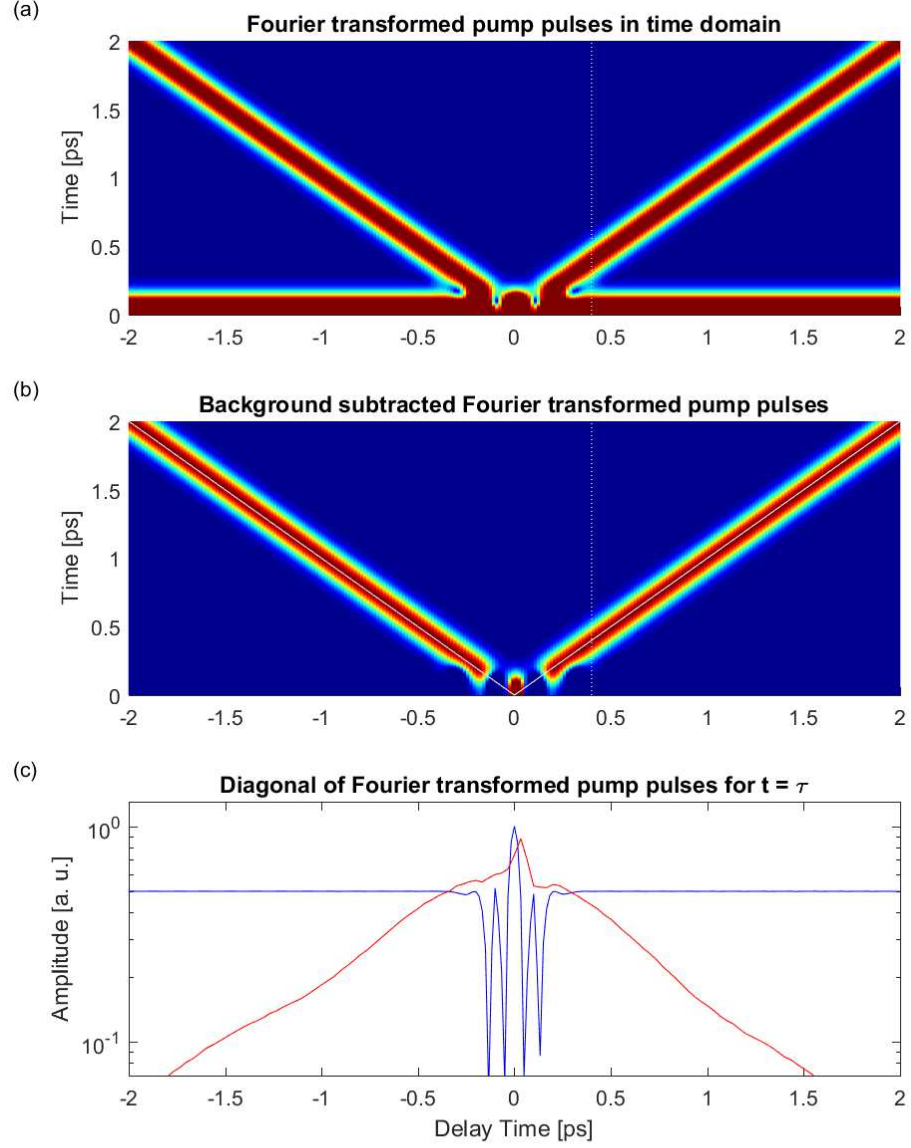


Figure 2.4: Simulated laser signal. (a) Numerical Fourier transform of two pump pulses delayed in time; dashed line corresponds to a $\tau = 0.4$ ps delay in Fig. 2.3.a-b. (b) Background subtracted numerical Fourier transform of Fig. 2.3.c. Dashed line corresponds to a $\tau = 0.4$ ps delay in Fig. 2.3.a-b, solid lines correspond to $t = \tau$. (c) Signal from diagonal of (b) where $t = \tau$ in blue. For comparison, in red: experimental data for the diagonal of a real laser at 371 nm collected by a non-ideal spectrometer.

The Stokes polarization density $S(\omega, \tau)$ is a convolution of the Raman gain and the incident intensity:

$$\begin{aligned} S(\omega, \tau) &= \int I(\omega - \omega_L + \omega') R(\omega') d\omega' + \int I(\omega - \omega_L + \omega') R(\omega') e^{i(\omega + \omega')\tau} d\omega' \\ &= \int I(\omega - \omega_L + \omega') R(\omega') d\omega' + e^{i\omega\tau} \int I(\omega - \omega_L + \omega') R(\omega') e^{+i\omega'\tau} d\omega'. \end{aligned} \quad (2.8)$$

For laser pulses that are much broader in frequency than the Raman gain linewidths so that the intensity $I(\omega)$ is approximately constant over $R(\omega)$, the signal can be approximated as

$$S(\omega, \tau) \sim I(\omega - \omega_L + \omega_1) \int R(\omega') d\omega' + e^{i\omega\tau} I(\omega - \omega_L + \omega_1) \int R(\omega') e^{i\omega'\tau} d\omega' \quad (2.9)$$

where ω_1 is a Raman shift. For a homogeneously broadened system we can write the Raman modes in the frequency domain as Lorentzians, which correspond in the time domain to

$$R(t) = \sum_i A_i e^{-\Gamma_i t} e^{i\omega_i t + i\phi_i} + c.c. \quad (2.10)$$

where Γ_i is the dephasing rate, ω_i is the Raman shift in frequency, and ϕ_i is the phase of the mode. We assume that the integral over all of the Raman gain is 1. We then find the signal for a particular mode to be

$$\begin{aligned} S_i(\omega, \tau) &\sim A_i I_i(\omega) + e^{i\omega\tau} A_i I_i(\omega) e^{-\Gamma_i |\tau|} e^{-i\omega_i \tau} \\ &\sim A_i I_i(\omega) (1 + e^{-\Gamma_i |\tau|} e^{i(\omega - \omega_i)\tau + i\phi_i}) \end{aligned} \quad (2.11)$$

where we have written $I_i(\omega) = I(\omega - \omega_L + \omega_i)$, ϕ_i is the relative phase between the Raman coherence and the incident pulses and we have omitted terms oscillating at $\omega + \omega_i$.

When there are two Stokes modes, one centered at ω_1 and the other at ω_2 , the signal becomes

$$S(\omega, \tau) \sim A I_1(\omega) (1 + e^{-\Gamma_1 |\tau|} e^{i(\omega - \omega_1)\tau + i\phi_1}) + B I_2(\omega) (1 + e^{-\Gamma_2 |\tau|} e^{i(\omega - \omega_2)\tau + i\phi_2}). \quad (2.12)$$

For our analysis we subtract the background signal, which corresponds to

$$I_{bgd}(\omega, \tau \rightarrow \infty) = A I_1(\omega) + B I_2(\omega). \quad (2.13)$$

This background is taken by methods described in the previous section. This makes the background-subtracted Stokes polarization signal

$$S(\omega, \tau) \sim AI_1(\omega)e^{-\Gamma_1|\tau|}e^{i(\omega-\omega_1)\tau+i\phi_1} + BI_2(\omega)e^{-\Gamma_2|\tau|}e^{i(\omega-\omega_2)\tau+i\phi_2}. \quad (2.14)$$

The detected signal on the spectrometer is the absolute value of $S(\omega, \tau)$. For the data analysis we take the Fourier transform

$$S(t, \tau) = \int_{-\infty}^{\infty} S(\omega, \tau)e^{-i\omega t}d\omega \quad (2.15)$$

and consider only the signal for $\tau = t$, see Fig. 2.6.c. For simplicity, we keep the complex form of Eq. 2.14 and obtain

$$S(t) \sim Ae^{-\Gamma_1|t|}e^{-i\omega_1 t+i\phi_1} + Be^{-\Gamma_2|t|}e^{-i\omega_2 t+i\phi_2}. \quad (2.16)$$

Taking the absolute value squared, we find

$$|S(t)|^2 \sim A^2e^{-2\Gamma_1|t|} + B^2e^{-2\Gamma_2|t|} + 2ABe^{-(\Gamma_1+\Gamma_2)|t|}\cos((\omega_2 - \omega_1)|t| + (\phi_2 - \phi_1)), \quad (2.17)$$

and then the absolute value which is the Fourier-transform of the signal we measure, is

$$|S(t)| \sim [A^2e^{-2\Gamma_1|t|} + B^2e^{-2\Gamma_2|t|} + 2ABe^{-(\Gamma_1+\Gamma_2)|t|}\cos((\omega_2 - \omega_1)|t| + (\phi_2 - \phi_1))]^{1/2} \quad (2.18)$$

where $(\phi_2 - \phi_1)$ is the phase difference between the two modes at $t = 0$ (when the laser pulse is incident). Here we find that by allowing n modes in Eq. 2.10, the complete TCUPS signal is

$$|S(t)| \sim \left[\sum_i A_i^2 e^{-2\Gamma_i|t|} + \sum_{i \neq j} 2A_i A_j e^{-(\Gamma_i+\Gamma_j)|t|} \cos((\omega_j - \omega_i)|t| + (\phi_j - \phi_i)) \right]^{1/2}. \quad (2.19)$$

To compare the two mode signal with the CARS signal from [12],

$$I_{CARS}(t) \sim |Ae^{-t/T_2'} + Be^{i\Delta\omega t - t/T_2'' + i\phi}|^2 \quad (2.20)$$

we change variables in their equation to $T'_2 = 1/\Gamma_1, T''_2 = 1/\Gamma_2, \Delta\omega = \omega_2 - \omega_1$, and $\phi = \phi_2 - \phi_1$:

$$I_{CARS}(t) \sim |Ae^{-\Gamma_1 t} + Be^{i(\omega_2 - \omega_1)t - \Gamma_2 t + i(\phi_2 - \phi_1)}|^2 \quad (2.21)$$

which when expanded equates to

$$I_{CARS}(t) \sim A^2 e^{-2\Gamma_1 t} + B^2 e^{-2\Gamma_2 t} + 2AB e^{-(\Gamma_1 + \Gamma_2)t} \cos((\omega_2 - \omega_1)t + (\phi_2 - \phi_1)). \quad (2.22)$$

This is the same as equation 2.17 for positive t ; note that the CARS signal is squared, while the TCUPS signal is not [4].

2.2.2 Quantum derivation

Alternatively, as we are in the single-excitation regime we can derive the signal in terms of the wave function. We start with the expression for the complete light and matter wave function for a single excitation state, which is a combination of the matter state ψ and photonic state ϕ :

$$|\Psi\rangle = \frac{1}{\sqrt{2}} \left[|\psi(\tau)\rangle |\phi(\tau)\rangle + |\psi(0)\rangle |\phi(0)\rangle \right] \quad (2.23)$$

The matter state at a time τ can be written

$$|\psi(\tau)\rangle = a(\tau)|\psi(0)\rangle + b(\tau)|\psi_\perp(\tau)\rangle \quad (2.24)$$

where $|\psi_\perp(\tau)\rangle$ is a state orthogonal to the initial state, $\langle\psi(0)|\psi_\perp(\tau)\rangle = 0$, and $a(\tau), b(\tau)$ are the probability amplitudes for being in the initial state and some orthogonal state (representing decay to the bath), respectively. Putting this into equation 2.23, we have

$$|\Psi\rangle = \frac{1}{\sqrt{2}} \left[|\psi(0)\rangle \left(|\phi(0)\rangle + a(\tau)|\phi(\tau)\rangle \right) + b(\tau)|\psi_\perp(\tau)\rangle |\phi(\tau)\rangle \right]. \quad (2.25)$$

The trace of the density matrix over the matter degrees of freedom is then

$$\begin{aligned} \rho_\phi &= \text{Tr}_\psi |\Psi\rangle \langle \Psi| \\ &= \frac{1}{2} \left[\left(|\phi(0)\rangle + a(\tau)|\phi(\tau)\rangle \right) \left(\langle\phi(0)| + a(\tau)\langle\phi(\tau)| \right) + |b(\tau)|^2 |\phi(\tau)\rangle \langle\phi(\tau)| \right] \end{aligned} \quad (2.26)$$

which becomes

$$\begin{aligned}\rho_\phi = & \frac{1}{2}|\phi(0)\rangle\langle\phi(0)| + \frac{|a(\tau)|^2 + |b(\tau)|^2}{2}|\phi(\tau)\rangle\langle\phi(\tau)| \\ & + \frac{a^*(\tau)}{2}|\phi(0)\rangle\langle\phi(\tau)| + \frac{a(\tau)}{2}|\phi(\tau)\rangle\langle\phi(0)|\end{aligned}\quad (2.27)$$

where $|a(\tau)|^2 + |b(\tau)|^2 = 1$. The evolution of the photonic state ϕ is given by

$$\begin{aligned}\langle\omega|\phi(\tau)\rangle &= e^{-i\omega'\tau}\langle\omega|\phi(0)\rangle \\ &= f(\omega')e^{-i\omega'\tau}\end{aligned}\quad (2.28)$$

with $f(\omega)$ is the pulse envelope, and $\omega' = \omega - \omega_L + \omega_i$, where ω_L is the laser frequency and ω_i is the Raman shift.

The signal is given by the expectation value of the density operator in the photonic basis $|\omega\rangle$:

$$I(\omega) = \langle\omega|\rho_\phi|\omega\rangle = |f(\omega')|^2 + \frac{a^*(\tau)}{2}e^{i\omega'\tau}|f(\omega')|^2 + \frac{a(\tau)}{2}e^{-i\omega'\tau}|f(\omega')|^2 \quad (2.29)$$

Noting that the amplitude $a(\tau)$ can be written

$$a(\tau) \equiv |a(\tau)|e^{i\theta} \quad (2.30)$$

we find

$$I(\omega) = |f(\omega')|^2(1 + |a(\tau)|\cos(\omega'\tau + \theta)) \quad (2.31)$$

which agrees with equation 2.11, given that $a(\tau)$ represents the coherence [35, 69], see Fig. 2.5.c for a single mode. Note that transient coherent spontaneous Raman scattering can be used to determine θ , the phase of the coherence relative to the incident pulses, unlike CARS.

Thus, using the above scheme to probe the single excitation coherence, we expect to observe oscillations of the photon interference visibility at the frequency difference between the states. Hence the TCUPS technique can be used to create a single collective excitation in a superposition state of multiple vibrational modes and observe the coherence evolution.

2.2.3 Simulations

To help with understanding the TCUPS signal we simulated the interaction and collection of the data in Matlab. A walkthrough with the explicit code can be found in Appendix C. We start with the laser pulses, shown in Fig. 2.3.a. One pulse is always centered at $t = 0$ and the other is delayed or advanced by some time τ seen in Fig. 2.3.a, corresponding to Eq. 2.5. Fig. 2.3.b shows how that time-domain plot of the laser pulses translates to the spectral intensity Eq. 2.7, which is what we see on the spectrometer. Fig. 2.3.c shows the spectral intensity for a series of time delays.

Following the analytical procedure described in the previous section, we then take the Fourier transform of the spectrum to convert from the frequency domain to the time domain. Fig. 2.4.a shows the complete real part of the transformed laser signal. After removing background by subtracting a far ($\tau > 20$ ps) spectrum we are left with Fig. 2.4.b. The spot that appears at center of the x-axis is due to the numerical coding used to simulate this data. The same feature (oscillation along the x-axis) shows up in all of these simulation results and can be ignored.

Taking the $t = \tau$ diagonal of Fig. 2.4.b, we arrive at Fig. 2.4.c. Since this computation assumes an ideal spectrometer with unlimited resolution we expect the signal away from $\tau = 0$ ps to be constant. For comparison to a real laser and spectrometer, the red curve in the figure is the laser pump at 371 nm used in the collection for the double mode signal found in the following chapter.

We generate a Raman response tensor for a single-mode system with parameters chosen to be similar to the single 1033 cm^{-1} mode investigated in methanol (see Appendix C) and take the Fourier transform to find the result in Fig. 2.5.a. We see here because of the low amplitude of the response the numerical relic along the x-axis is stronger. After removing the background from the simulated data, Fig. 2.5.b-c show the expectation for a single mode, which has the form of an exponential decay. Fig. 2.5.b also shows other orders of the numerical Fourier transform, although faintly, along the x-axis and as two diagonals above the main $t = \tau$ line. Taking the result here along the main diagonal of the figure we have Fig. 2.5.c, where the blue curve shows

the simulated result, and for comparison the red curve is a real data result which we'll discuss further in Ch. 3.

The second system we look at is two vibrational modes in Fig. 2.6 with parameters that are close to methanols 2835 and 2945 cm^{-1} modes. Again, in Fig. 2.6.a we see background along the x-axis to remove, the result which is shown in Fig. 2.6.b. Here we see coherence beating between two modes as an evenly spaced oscillation along the main diagonal $t = \tau$. We also see the other orders of the Fourier transformed signal and these too exhibit the coherence oscillation beating. The combination of the different orders of the transformed signal, and the numerical relic on the x-axis yield an artifact near the zero delay time, however this area of the two-dimensional time domain space can be ignored as it lies off of the $t = \tau$ diagonal. Fig. 2.6.c shows the main diagonals of the background-subtracted two-dimensional time domain plot in blue. For comparison an example of the data collected for the 2835 and 2945 cm^{-1} modes in liquid methanol is in red. Refer to Eq. 2.19 for the functional behavior of the signal.

Finally, in Fig. 2.7 we simulate a three-mode system, with parameters that correspond approximately to the 2884, 2925, and 2975 cm^{-1} modes in liquid propanol. Fig. 2.7.a shows the simulated result with background signal, Fig. 2.7.b shows the simulated result after the background has been removed. In Fig. 2.7.b we can still see evidence of the other orders the Fourier transformation and the numerical relic on the x-axis near zero delay which should still be ignored. Fig. 2.7.c shows the main diagonals of the corresponding two-dimensional time domain plot above it, in blue. For a qualitative comparison to data collected by the experiment, an experimental signal is shown in red. Further discussion of this system will be presented after the experimental results in Ch. 3.

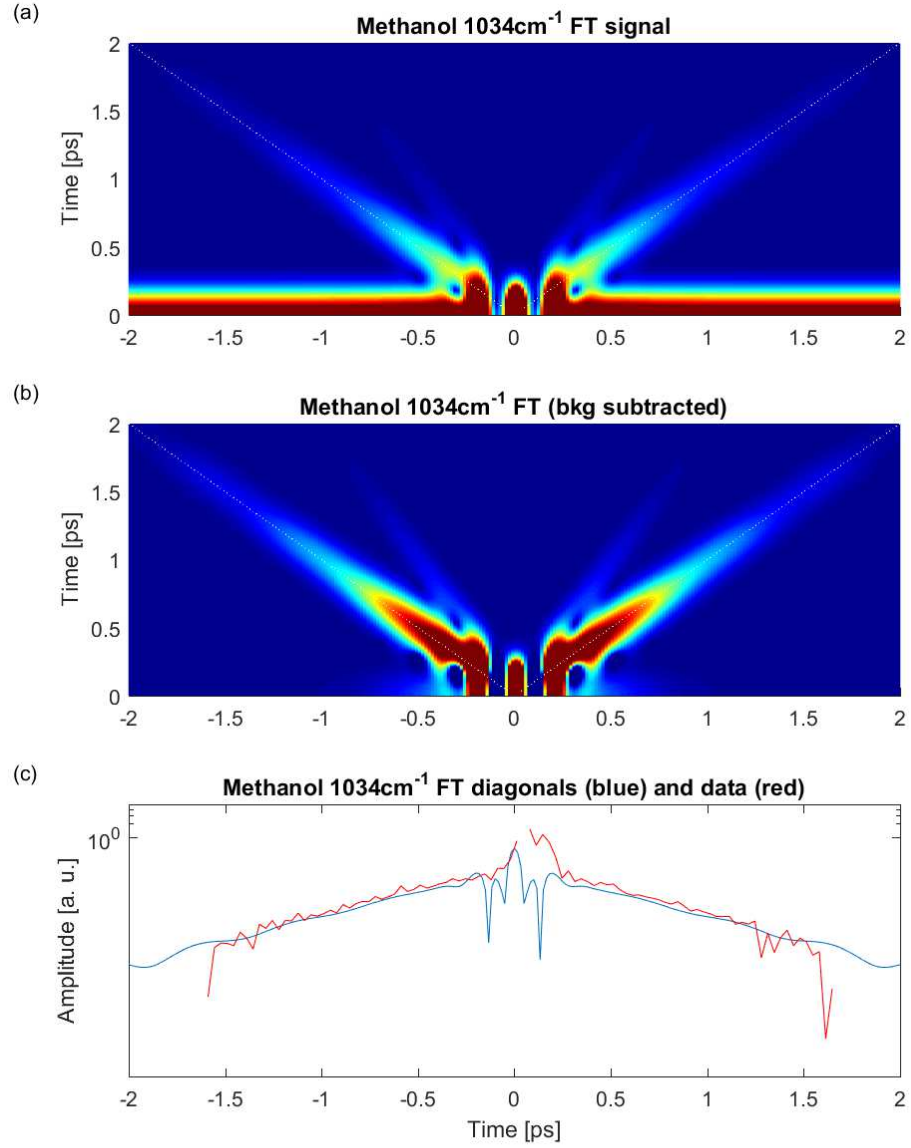


Figure 2.5: Matlab simulation output for a single mode. (a) Fourier transformed simulated signal for a single mode. (b) Background along the x-axis is removed from (a). (c) Diagonal of (b) where $t = \tau$. We see a computational residue in the form of a small oscillation. This is caused by the specific settings used in the simulation process and can be ignored.

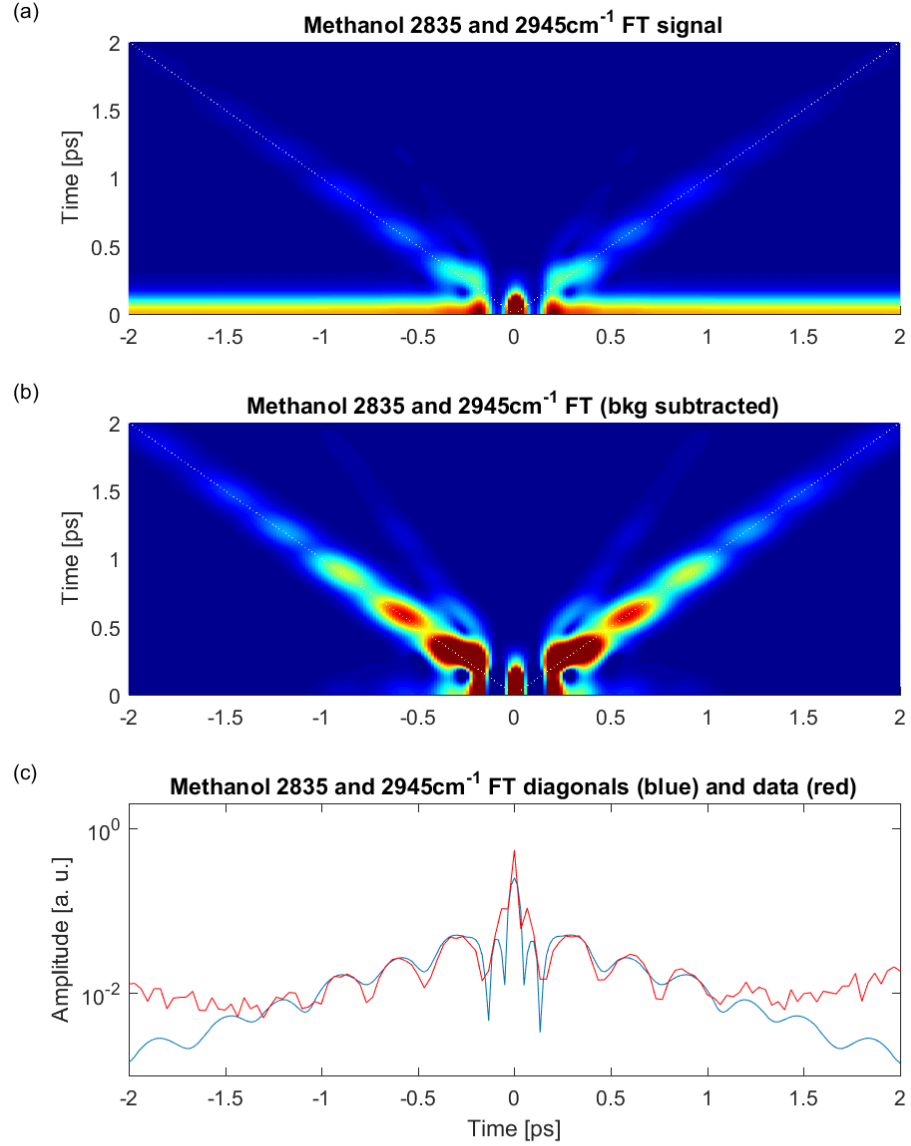


Figure 2.6: Matlab simulation output for two modes. Modes were chosen to approximately match methanol's 2835 and 2945 cm⁻¹ vibrations characteristic values. (a) Fourier transformed simulated signal for two modes. (b) Background along the x-axis is removed from (a). (c) Diagonal of (b) where $t = \tau$. The simulation shows a successful qualitative match to the experimental data.

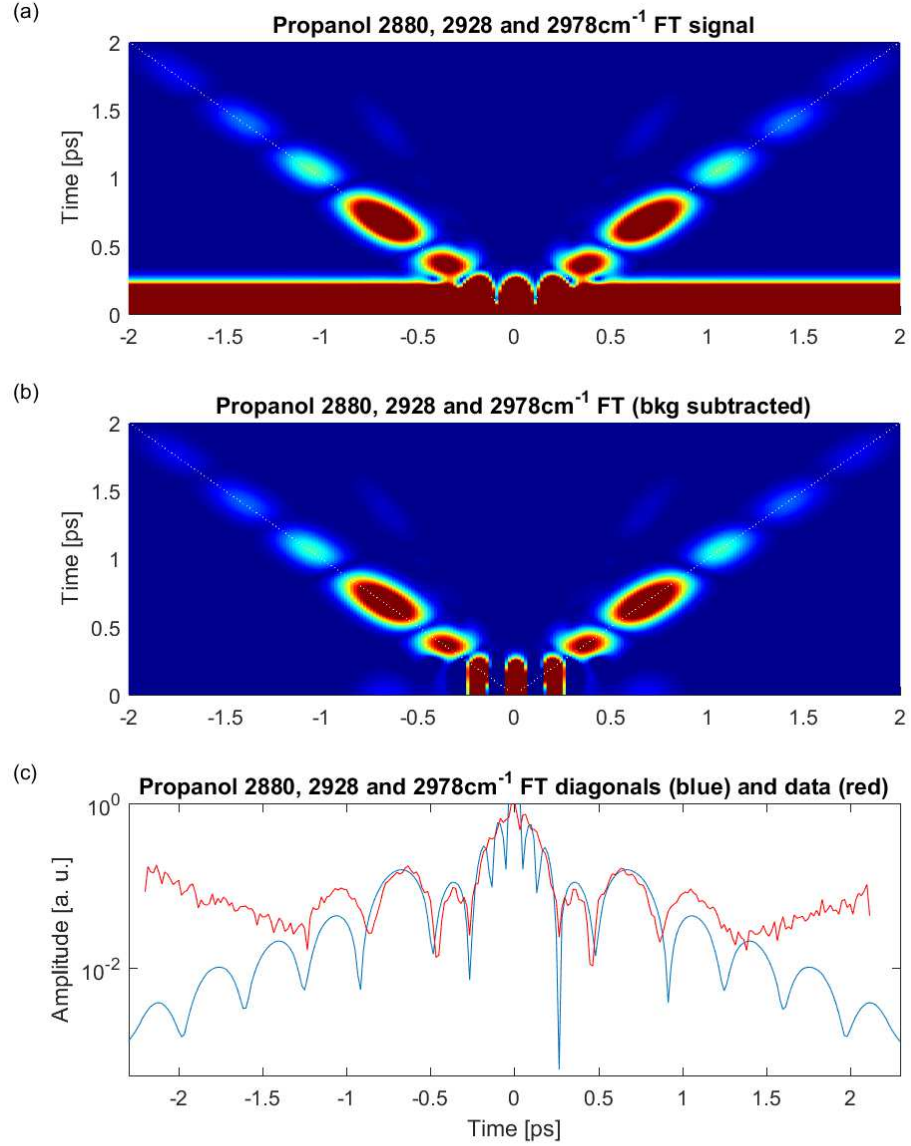


Figure 2.7: Matlab simulation output for three modes. Modes were chosen to approximately match propanol's 2884, 2925 and 2975 cm⁻¹ vibrations characteristic values. (a) Fourier transformed simulated signal for three modes. (b) Background along the x-axis is removed from (a). (c) Diagonal of (b) where $t = \tau$. We see that the simulation provides a good analogue for the experimental data.

Chapter 3

TCUPS IN SIMPLE ALCOHOLS

Using the setup outlined in Section 2.1, the Newport motion controller and the Andor iDus camera were operated through National Instruments' LabView software. The range of the spectrum of the Andor Shamrock spectrometer was specified to include the pump signal or the Stokes signal for a given data acquisition. The length of time photons were counted selected to be 2 s for most acquisitions. The step size was ~ 33 fs and the number of steps the linear motion stage would execute was set between 200-500 steps for most recordings. Ten data sets were then averaged after the full analysis for the final fitting.

Waldermann *et al.* had fine enough wavelength resolution to take a small portion of the Stokes spectrum and fit a sinusoid to their data to retrieve the decaying amplitudes of the diamond phonon coherence [35]. So initially we set out to measure the amplitude of the interference signal by a similar method. The background subtracted data collected in Fig. 3.1 was taken using a 2 s acquisition time, a 300 lines/mm grating in the spectrometer, a laser center wavelength of 780 nm, in room temperature methanol. Even though we were able to capture the laser wavelength (fits in red) as well as the two Raman modes (fits in green and blue) of interest, the shape of the signal was not uniform. This irregularity meant fitting the interference by hand was cumbersome, and inaccurate, leaving us with a need to find another method for analysis of the TCUPS signal.

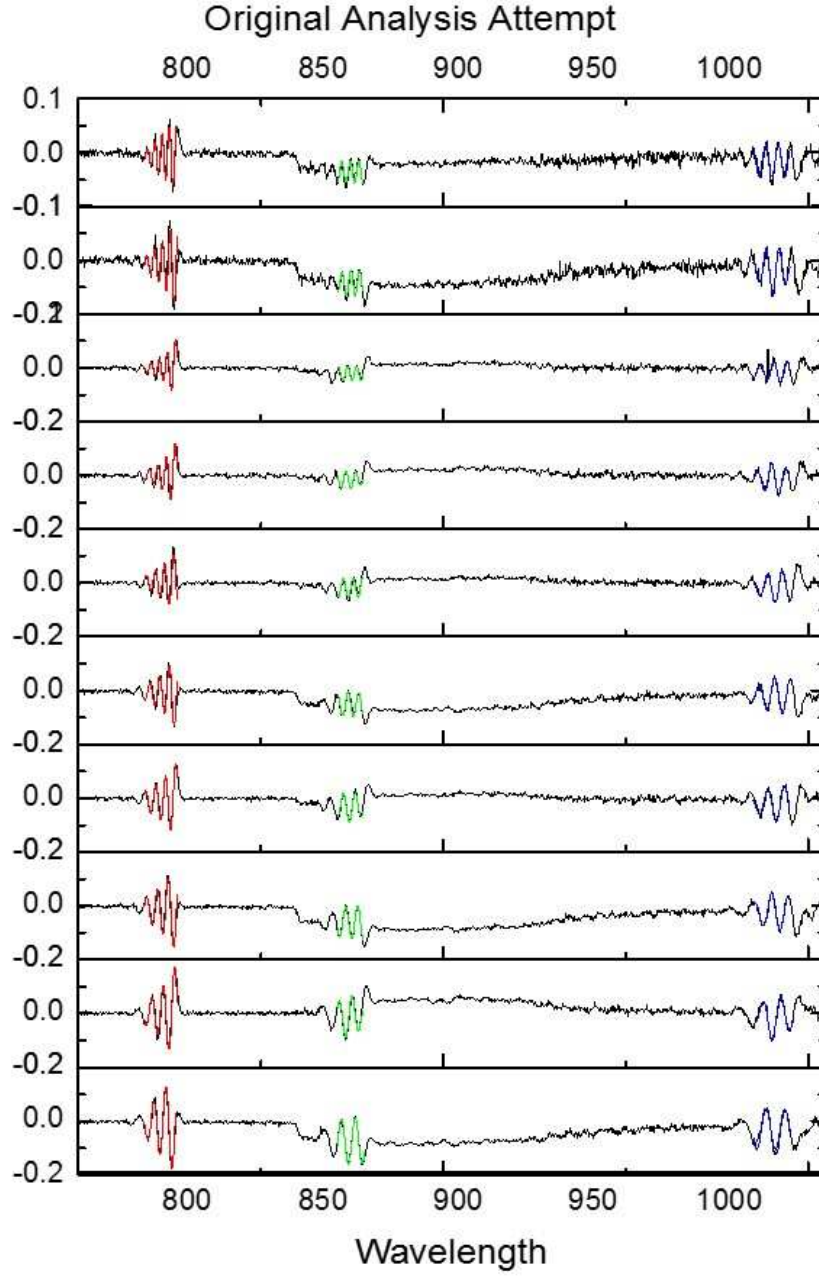


Figure 3.1: An example of a first attempt at measuring the amplitudes of the interference signal on the Stokes emission from liquid methanol for time delays, from top to bottom, of $\tau = 0.3167$ ps to $\tau = 0.1667$ ps in steps of 0.0167 ps. Pump fit (red), 1033 cm^{-1} mode fit (green), and $\sim 2900\text{ cm}^{-1}$ mode fit (blue).

This analytic hurdle was overcome by the Fourier analysis method set forth in the derivation of Eq. 2.19. Since we are using a real spectrometer we must also account for its limited resolving capabilities. A non-ideal spectrometer suffers from resolution variance at different wavelengths. To correct for this we assume a constant resolving power

$$R = \frac{\lambda}{\Delta\lambda} = \frac{C}{\lambda} \quad (3.1)$$

where λ is a specific wavelength, $\Delta\lambda$ is the smallest difference in wavelengths that can be distinguished at that λ , and C is a constant dependent on the width of the grating and the geometry in use in the spectrometer [70]. For the wavelengths used in the experiments, the resolving power is approximately the same. So for the laser and Stokes wavelengths, λ_L and λ_S ,

$$R_L = \frac{C}{\lambda_L} \sim R_S = \frac{C}{\lambda_S}. \quad (3.2)$$

Solving for C ,

$$C = \lambda_S R_S \sim \lambda_L R_L. \quad (3.3)$$

To find the ratio

$$\frac{\Delta\lambda_S}{\Delta\lambda_L}, \quad (3.4)$$

we write

$$\frac{\lambda_S}{\Delta\lambda_S} = \frac{\lambda_L R_L}{\lambda_S}. \quad (3.5)$$

Then

$$\frac{\lambda_S^2}{\lambda_L} = \Delta\lambda_S R_L. \quad (3.6)$$

Finally by replacing $R_L = \lambda_L/\Delta\lambda_L$ we have

$$\left(\frac{\lambda_S}{\lambda_L}\right)^2 = \frac{\Delta\lambda_S}{\Delta\lambda_L}. \quad (3.7)$$

This scaling factor is applied to each pump signal after the Fourier transformation in time to address the change in resolution between the pump and Stokes center wavelengths. The Stokes signal is then divided by the scaled pump signal to account for visibility decay due to finite spectrometer resolution.

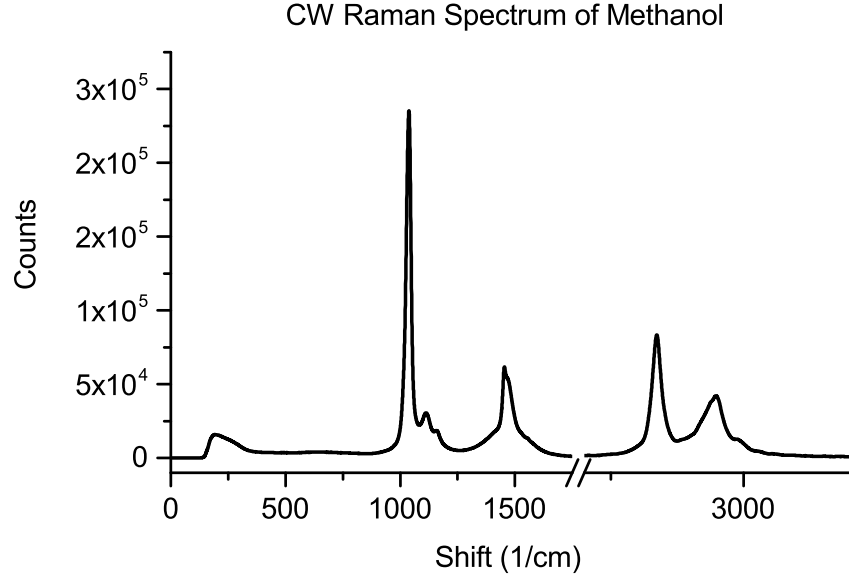


Figure 3.2: CW spectrum of liquid methanol taken with the help of Dr. Bruce Chase in the U. of Delaware’s I.S.E. Advanced Materials Characterization Lab. This spectrum was taken with a ten second exposure length, dark count subtraction, and the CW laser wavelength was 784.761 nm.

For comparison with TCUPS results, CW Raman spectra were taken independently with the help of Dr. Bruce Chase and the Advanced Materials Characterization Lab, shown in Figs. 3.2 and 3.3. The spectra were taken with a laser wavelength of 784.761 nm, with dark counts subtracted, and had a total exposure length of 10 s. This was helpful in providing a check and guide for the expected linewidths and difference frequencies for the Raman shifts investigated. Peak fitting, shown in Fig. 3.4, 3.5, and 3.6, was done through the use of the software Origin using a Pearson VII peak fitting function,

$$y = y_0 + \frac{2A\Gamma(m)\sqrt{2^{(1/m)} - 1}}{(\sqrt{\pi}w\Gamma(m - 0.5))} \left(1 + \frac{4(2^{(1/m)} - 1)}{w^2}(x - xc)^2 \right)^{(-m)}. \quad (3.8)$$

The fit results are summarized in Tables 3.1, 3.2, and in 3.3 and 3.4.

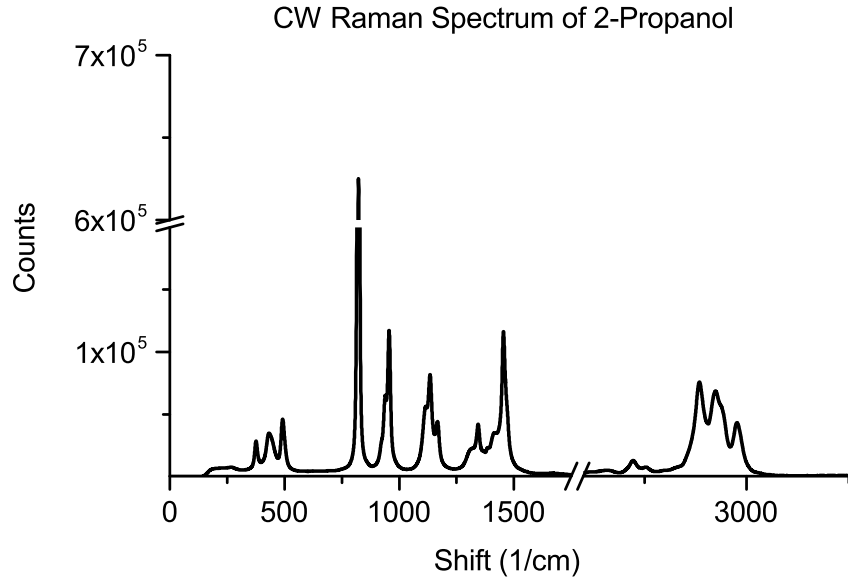


Figure 3.3: CW spectrum of liquid 2-propanol taken with the help of Dr. Bruce Chase in the U. of Delaware’s I.S.E. Advanced Materials Characterization Lab. This spectrum was taken with a ten second exposure length, dark count subtraction, and the CW laser wavelength was 784.761 nm.

3.1 Single Resonance - Methanol

The Stokes spectrum for the single mode in methanol, 1033 cm^{-1} shift, was recorded with the laser pulse centered at 790 nm. The filtering used for this data collection can be found in Appendix A. For a general comparison of this Raman shift to the others of interest Fig. 3.2 shows the strongest features of the CW Raman spectrum for methanol between 250 to 3200 cm^{-1} . The 1033 cm^{-1} vibrational mode is fitted with a Pearson VII function in Fig. 3.4. As seen in the figure, there does exist a small nearby mode; however, due to the integrated amplitude difference between this small shoulder mode and the mode of interest, we expect minimal interference of the expected TCUPS signal.

The resolution of the spectrometer for the pump in this case was very good, as seen in Fig. 3.7. In Fig. 3.7.a-c the laser pulse spectrum is shown for example time delays showing that as the delay time τ between the pulse increases the spectral fringe spacing decreases as expected. Fig. 3.7.d shows all of the recorded pump spectra for a

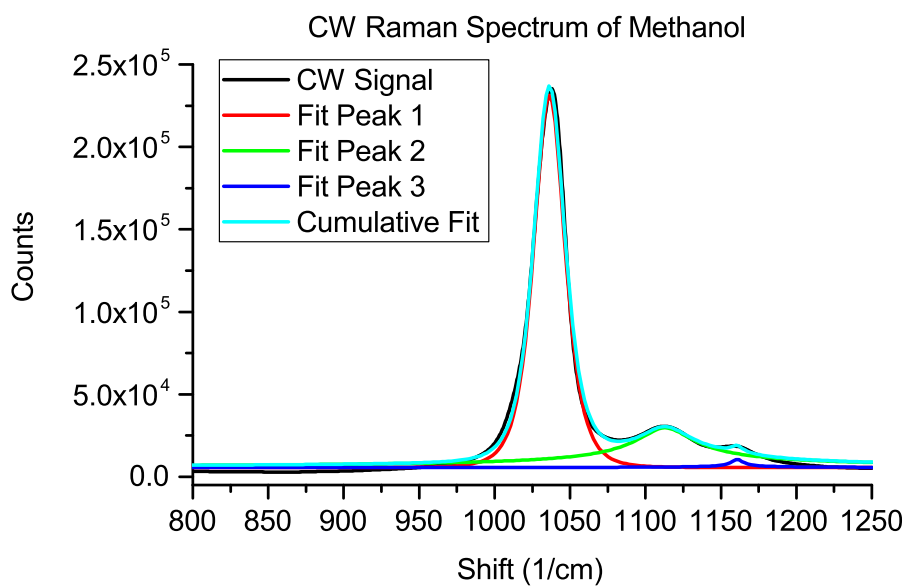


Figure 3.4: 800-1250 cm^{-1} spectral region of liquid methanol. The peak-fitting used a Pearson VII function, Eq. 3.8, parameters can be found in Table 3.1.

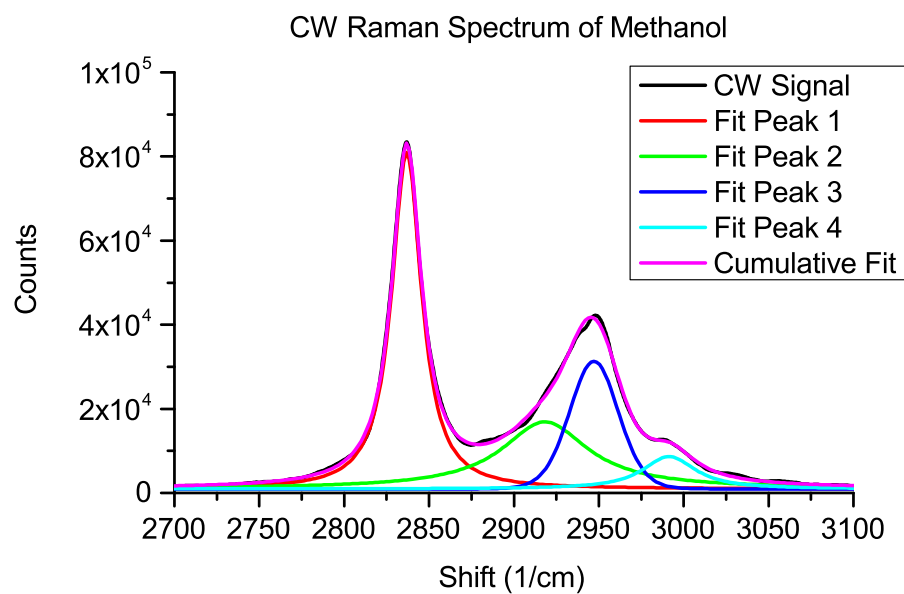


Figure 3.5: 2700-3100 cm^{-1} spectral region of liquid methanol. The peak-fitting used a Pearson VII function, parameters can be found in Table 3.2.

Three mode Pearson VII Fitting of 800-1250 cm^{-1} in methanol

		Reduced Chi-Sqr	7.5E7
		Adj. R-Square	0.87
		Value	
Peak1	y0	5551	± 358
	xc	1036.27	$\pm 0.084 \text{ cm}^{-1}$
	A	6.55E6	± 95477
	w	24.36	$\pm 0.27 \text{ cm}^{-1}$
	m	2.34	± 0.21
Peak2	y0	5551	± 358
	xc	1113.01	$\pm 1.76 \text{ cm}^{-1}$
	A	1.78E9	$\pm 6.68\text{E}10$
	w	62.14	$\pm 10.75 \text{ cm}^{-1}$
	m	0.5	± 0.009
Peak3	y0	5551	± 358
	xc	1160.76	$\pm 4.49 \text{ cm}^{-1}$
	A	3.31E17	$\pm 1.43\text{E}20$
	w	12.21	$\pm 17.21 \text{ cm}^{-1}$
	m	0.5	$\pm 2.29\text{E}-11$

Table 3.1: Pearson VII fitting of the 800-1250 cm^{-1} region of liquid methanol using the equation Eq. 3.8. The peak fitting was done through the software Origin. The width, w, for Peak1 corresponds to a ~ 1.4 ps lifetime. This value is approximate.

Four mode Pearson VII Fitting of 2700-3100 cm^{-1} in methanol

		Reduced Chi-Sqr	2.1E5
		Adj. R-Square	0.99
		Value	
Peak1	y0	956	± 15.9
	xc	2836.82	$\pm 0.019 \text{ cm}^{-1}$
	A	2.51E6	± 16423
	w	21.03	$\pm 0.048 \text{ cm}^{-1}$
	m	1.08	± 0.01
Peak2	y0	956	± 15.9
	xc	2918.24	$\pm 30.4 \text{ cm}^{-1}$
	A	1.64E6	$\pm 1.26\text{E}6$
	w	62.45	$\pm 14.35 \text{ cm}^{-1}$
	m	0.94	± 0.105
Peak3	y0	956	± 15.9
	xc	2947.1425	$\pm 5.23 \text{ cm}^{-1}$
	A	1.12E6	$\pm 9.1\text{E}5$
	w	33.89	$\pm 12.67 \text{ cm}^{-1}$
	m	9.34	± 26.55
Peak4	y0	956	± 15.9
	xc	2991.4	$\pm 1.5 \text{ cm}^{-1}$
	A	4.3E5	$\pm 3.9\text{E}5$
	w	37.44	$\pm 9.83 \text{ cm}^{-1}$
	m	1.073	± 0.63

Table 3.2: Pearson VII fitting of the 2700-3100 cm^{-1} region of liquid methanol using Eq. 3.8. The peak fitting was done through the software Origin. The widths, w, for Peak1 and Peak 3 correspond to a $\sim 1.6 \text{ ps}$ and $\sim 1 \text{ ps}$ lifetimes, respectively. These values are approximate. Since we are not suppressing the Peak2 and Peak4 signals through some selective means, these two add into the effective mode widths, shortening the expected lifetimes.

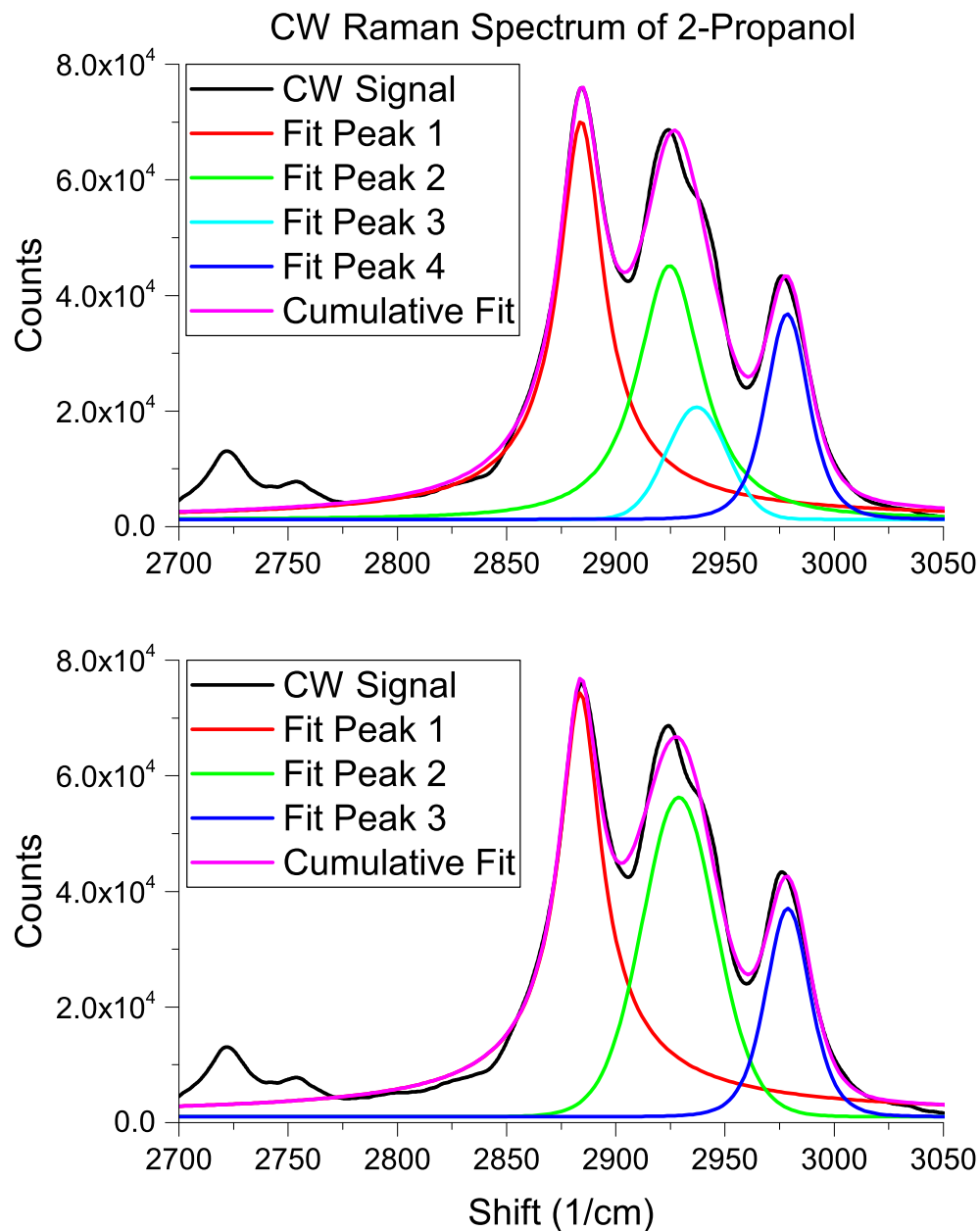


Figure 3.6: 2700-3050 cm^{-1} spectral region of liquid 2-propanol. The peak-fitting using a Pearson VII function, parameters can be found in Tables 3.3 and 3.4. We see that the four peak system (recently identified by [65]) is reasonably approximated by three peaks (historically this has been the case in the literature [57], etc.).

Four mode Pearson VII Fitting 2700-3050 cm^{-1} in 2-propanol

		Reduced Chi-Sqr	2.29E6
		Adj. R-Square	0.98
		Value	
Peak1	y0	1274	± 40.8
	xc	2884.14	$\pm 0.69 \text{ cm}^{-1}$
	A	4.46E6	$\pm 4.2\text{E}5$
	w	27.07	$\pm 0.40 \text{ cm}^{-1}$
	m	0.7	± 0.03
Peak2	y0	1274	± 40.8
	xc	2924.71	$\pm 5.83 \text{ cm}^{-1}$
	A	2.15E6	$\pm 1.58\text{E}6$
	w	34.94	$\pm 3.78 \text{ cm}^{-1}$
	m	1.23	± 0.45
Peak3	y0	1274	± 40.8
	xc	2937.09	$\pm 15.02 \text{ cm}^{-1}$
	A	6.7E5	$\pm 1.36\text{E}6$
	w	32.51	$\pm 27.40 \text{ cm}^{-1}$
	m	170	± 21893.26
Peak4	y0	1274	± 40.8
	xc	2978.53	$\pm 0.87 \text{ cm}^{-1}$
	A	9.58E5	$\pm 1.38\text{E}5$
	w	23.01	$\pm 1.84 \text{ cm}^{-1}$
	m	2.60	± 0.91

Table 3.3: Pearson VII fitting of the 2700-3050 cm^{-1} region of liquid 2-propanol using Eq. 3.8. The peak fitting was done through the software Origin.

Three mode Pearson VII Fitting of 2700-3050 cm^{-1} in 2-propanol

		Reduced Chi-Sqr	2.09E5
		Adj. R-Square	0.99
		Value	
Peak1	y0	956	± 15.9
	xc	2836.82	$\pm 0.02 \text{ cm}^{-1}$
	A	2.51E6	± 16423
	w	21.03	$\pm 0.05 \text{ cm}^{-1}$
	m	1.08	± 0.010
Peak2	y0	956	± 15.9
	xc	2918.24	$\pm 30.40 \text{ cm}^{-1}$
	A	1.64E6	$\pm 1.26\text{E}6$
	w	62.45	$\pm 14.36 \text{ cm}^{-1}$
	m	0.94	± 0.10
Peak3	y0	956	± 15.9
	xc	2947.14	$\pm 5.23 \text{ cm}^{-1}$
	A	1.12E6	± 909053
	w	33.89	$\pm 12.67 \text{ cm}^{-1}$
	m	9.34	± 26.55

Table 3.4: Pearson VII fitting of the 2700-3050 cm^{-1} region of liquid 2-propanol using Eq. 3.8. The peak fitting was done through the software Origin. The widths, w, for Peak1, Peak2, and Peak 3 correspond to ~ 1.6 ps, ~ 0.5 ps, and ~ 1 ps lifetimes, respectively. These value are approximate.

given data set, as a function of delay time τ .

The spectrometer suffers from an etaloning effect in the Stokes spectral range using the 1200 lines/mm grating. The signature of this effect can be seen in Fig. 3.8.a-d. The Raman signal in this region is dwarfed by this etaloning on the wings of the pulse, and while background subtraction simplifies the visible interference pattern on the laser spectrum, seen in Fig. 3.9, the background subtracted spectra for the Stokes signal in Fig. 3.10 still exhibits the etaloning as it is sensitive to the instantaneous intensity which varies between the time delay data and the background signal used for subtraction. Even though it is hard to find where the TCUPS signal might be in this region Fig. 3.10.d shows the signature interference patterning when all of the time delay spectra are plotted together for contrast.

The effect in the end did not prevent us from extracting the Stokes signal we are looking for; however, it did significantly lower the signal-to-noise ratio for this set of data. To address this, following the theoretical analysis outlined before, we take the Fourier transform of the spectra with respect to the frequency domain, and find the result for the laser signal in Fig. 3.11.a, and for the Stokes spectra in Fig. 3.11.b. The etaloning in the spectrometer caused an irregular amplitude signal along the line $\tau = 0$ for all t in the Stokes signal seen in the middle of Fig. 3.11.b, but as this is away from the signal of interest along $t = \tau$, the Fourier transform procedure has removed the degradation of the signal-to-noise ratio due to etaloning.

The line $t = \tau$ for the laser (in black) and for the Stokes (in red) signals are shown in Fig. 3.11.c. To account for the resolution of the spectrometer we divide the Stokes signal by the laser signal, shown in Fig. 3.11.d. There exists a peak near zero time delay that is caused by complete constructive interference in the Stokes spectra. When fitting the scaled data with our expected theoretical form in Eq. 2.19 we ignore these data points near zero delay; the fitted data is shown in Fig. 3.12. We find the data is well fit by an exponential decay; the fit parameters are shown in Table 3.5. The measured lifetime of 440 ps agrees with results from the CW Raman measurements presented in Fig. 3.4 and Table 3.1 and the literature [46].

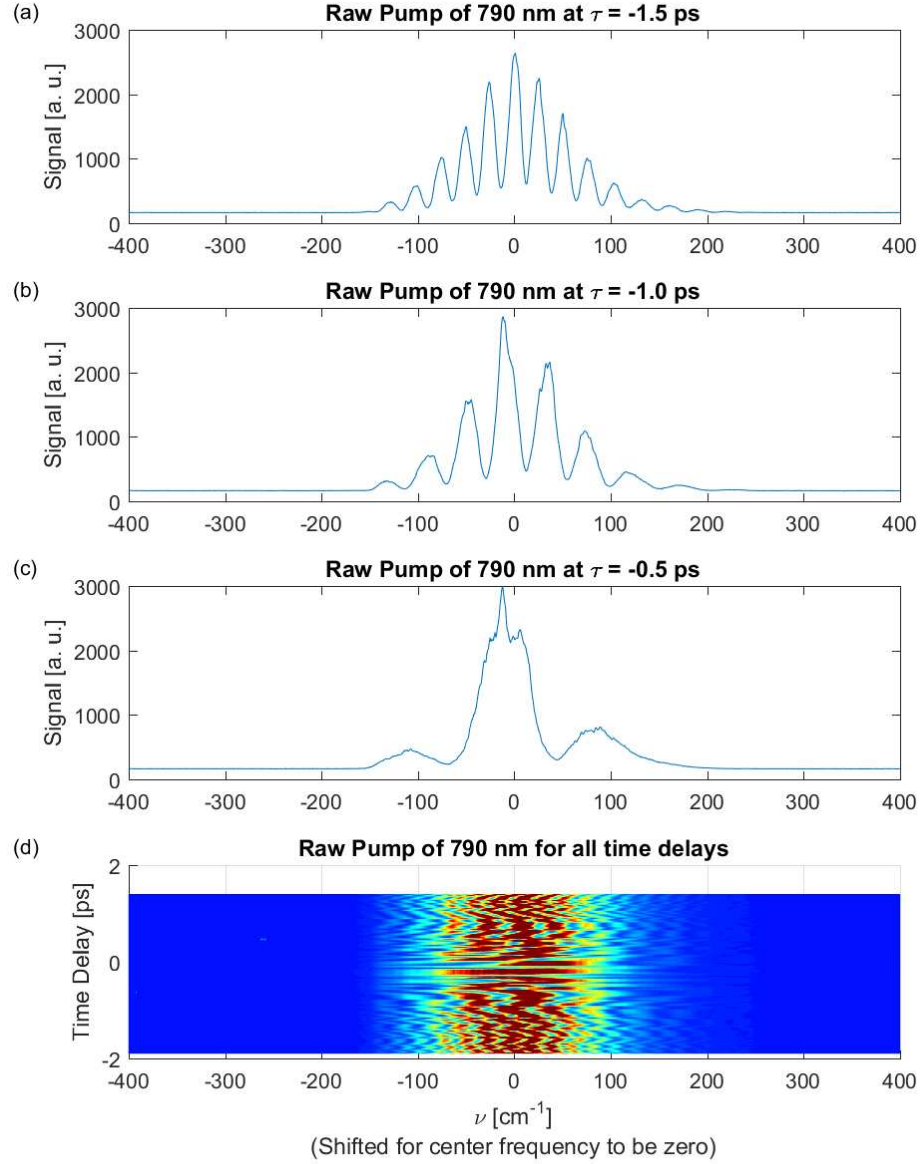


Figure 3.7: (a-c) Example of raw 790 nm pump spectra taken for various delay times. From these we see that the interference of the pump is not perfect, the fringes do not go to zero. This would affect the decay of the Stokes signal; however, we correct for this in the analysis. (d) Raw pump spectra for all recorded time delays of a single data set.

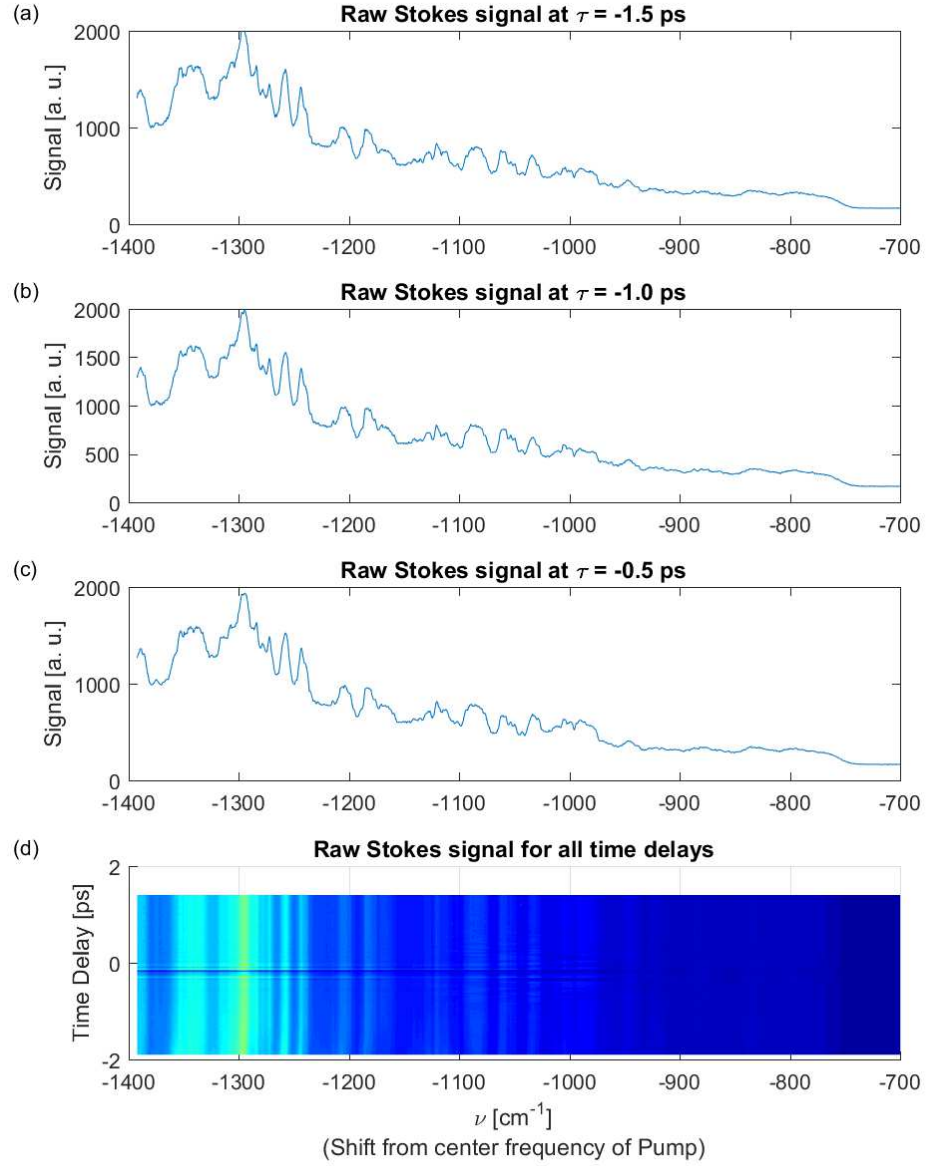


Figure 3.8: (a-c) Example of raw 1033 cm^{-1} Stokes spectrum taken for various delay times. (d) Raw Stokes spectra for all recorded time delays of a single data set. The Stokes signal in spectra we expect here is overshadowed by the etaloning effect from the spectrometer.

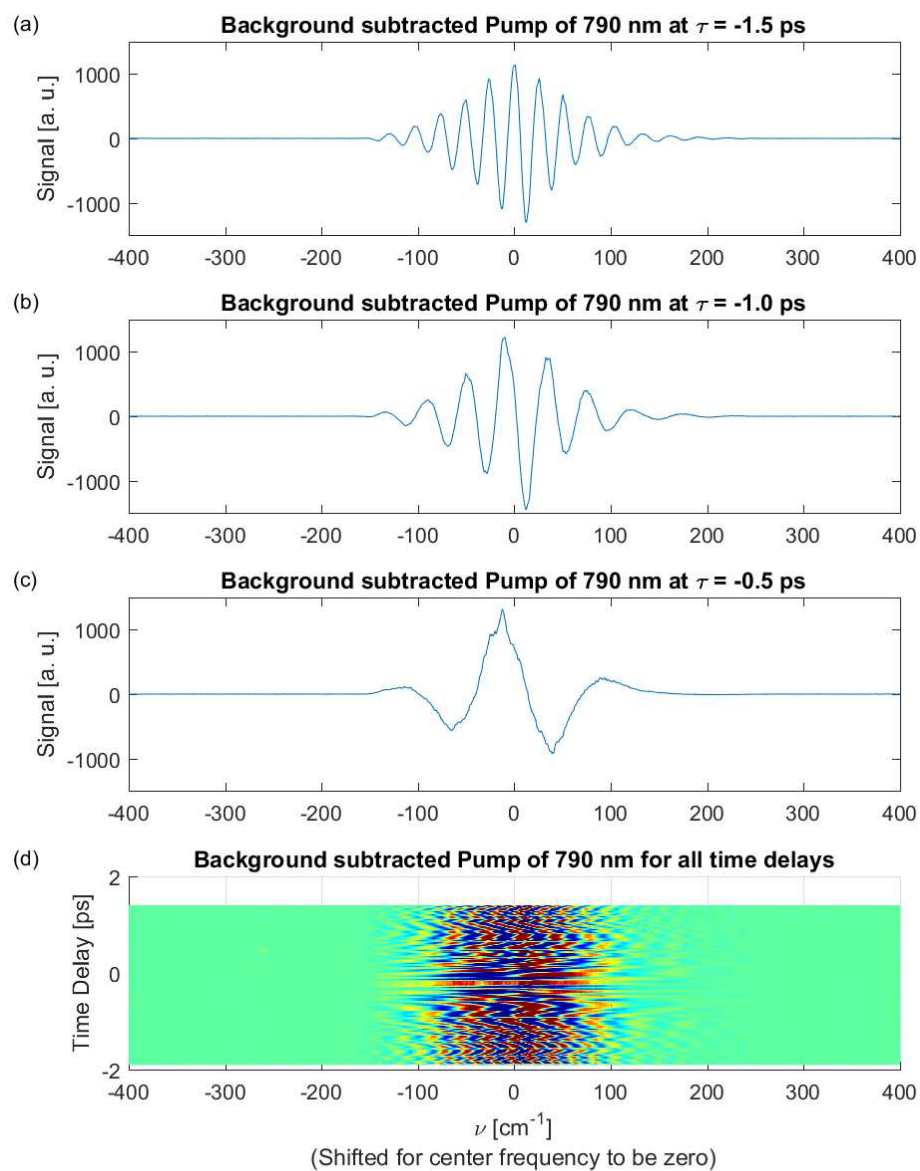


Figure 3.9: (a-c) Example of background subtracted 790 nm pump interference taken for various delay times. (d) Background subtracted pump spectra for all recorded time delays of a single data set.

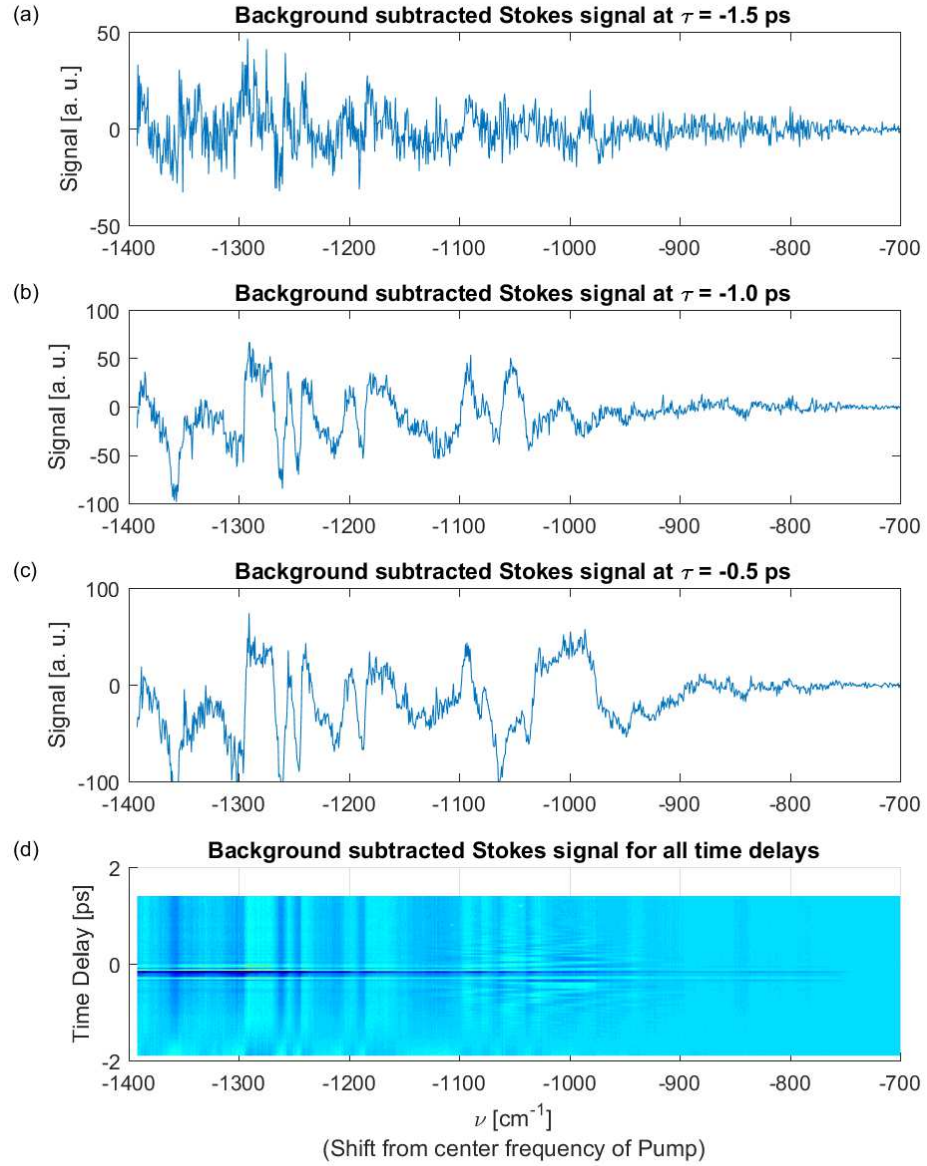


Figure 3.10: (a-c) Example of background subtracted 1033 cm $^{-1}$ Stokes interference taken for various delay times. (d) Background subtracted Stokes spectra for all recorded time delays for a single data set. It is evident in the center that the phase distortions of the interference signal are present, though still masked by the etaloning effect of the spectrometer.

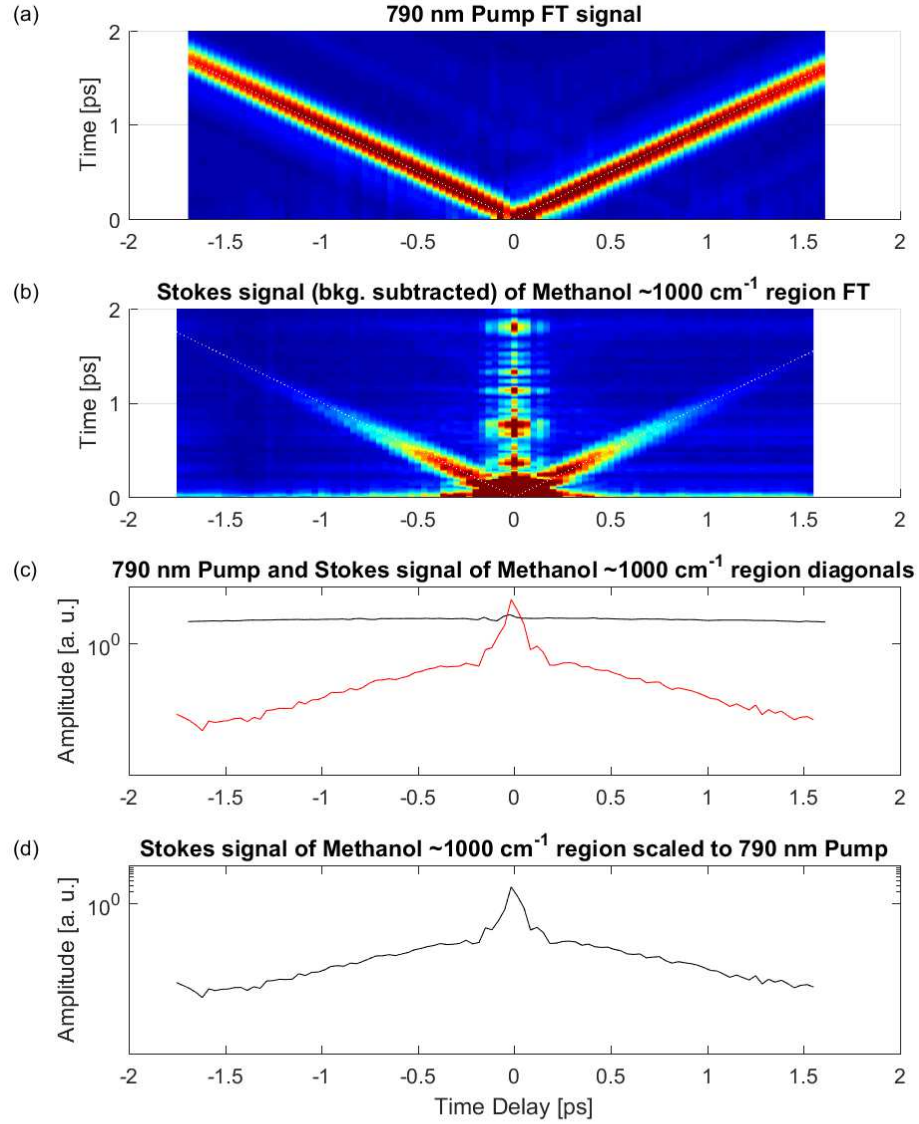


Figure 3.11: (a) Numerical Fourier Transformed pump signal. (b) Numerical Fourier Transformed Stokes signal, the amplitude in the center is due to the etaloning effect of the spectrometer. Dashed lines correspond to delay time $\tau = t$ the Fourier transform time coordinate. (c) Diagonals of pump and Stokes signal along the dashed lines. (d) Stokes signal scaled to pump. Since the signal we seek lies upon the line $\tau = t$, the etaloning effect does not influence our extracted signal.

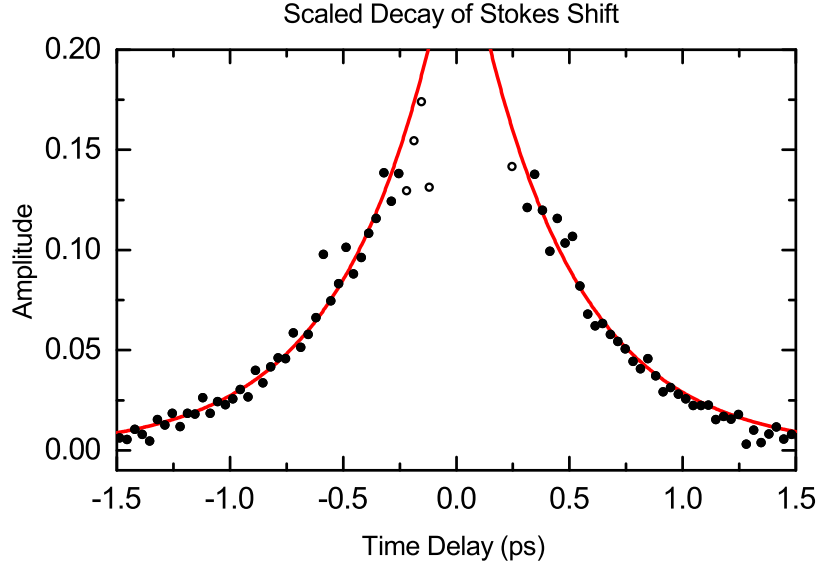


Figure 3.12: Scaled decay of 1033 cm^{-1} stokes signal as a function of time delay between pulses. Data points representing the average of the Fourier Transformed Stokes signal from multiple data sets taken sequentially, all scaled by their recorded pump spectra. Solid curve is a numerical fitting using Eq. 2.19 for a single mode, see Table 3.5.

Nonlinear fit for single mode 1033 cm^{-1} in methanol

Reduced Chi-Sqr 3.78E-5
Adj. R-Square 0.97

Parameter	Value
y_0	0 ± 0.003
A	0.27 ± 0.01
$1/\Gamma$	0.440 ± 0.026 ps
t_0	0.013 ± 0.005 ps

Table 3.5: Nonlinear fit parameters of Fig. 3.12 for the single mode, 1033 cm^{-1} shift, in methanol. The function used to fit was Eq. 2.19 where we added vertical and horizontal offsets y_0 and t_0 . The lifetime measured, $1/\Gamma$, agrees with CW linewidth measurements.

3.2 Double Resonance - Methanol

The TCUPS spectrum shown in Fig. 3.13 for a double mode system in methanol, $\sim 2900 \text{ cm}^{-1}$ shifts, was recorded with the laser pulse frequency doubled to 371 nm. The frequency doubling allowed us to use a magnitude lower of average incident pump power and still gain in the Raman emission counts, as the Raman response intensity is proportional to the fourth power of the pump frequency [71]. By making this conversion we gain a factor of 16 in amplitude and reduced the likelihood of boiling the liquid alcohol sample. The filtering used can be found in Appendix A and the delay time step size is still $\sim 33 \text{ fs}$.

In Fig. 3.13.a-c are various time delays showing the laser spectrum, with a frequency range large enough to also show the Stokes location in principle, the laser and Stokes spectra could be taken simultaneously; however, no Stokes signal is seen due to the filtering used, see Appendix A. Fig. 3.13.d shows all of the time delays taken for a single data set. The slightly non-Gaussian envelope is due to the second harmonic generation in the BiBO crystal that had uneven phase matching across the laser bandwidth. The removal of the background also shows this deformity in Fig. 3.15.a-d. The Fourier transformation of the laser signal in Fig. 3.17.a shows that the limited spectral resolution of the spectrometer at this wavelength makes the laser amplitude along the $t = \tau$ line decay more noticeably than before.

The resolution of the spectrometer for the pump in this case was much less than that for the 780 – 900 nm region; however, the spectrometer no longer suffered from an etaloning effect in the Stokes spectral range. Instead, a problem in this range is a broad fluorescence around $\sim 500 \text{ nm}$. The fluorescence effect can be seen in Fig. 3.14 and Fig. 3.16 as a shelf on which the interference of interest lies. The fluorescence itself also exhibits interference with a periodicity following the interference of the laser pulses; however, the lifetimes of the fluorescing states are much longer than the lifetime of the vibrational modes, and thus this results in a constant background, evident along the main diagonal of the Stokes signal in Fig. 3.17.b.

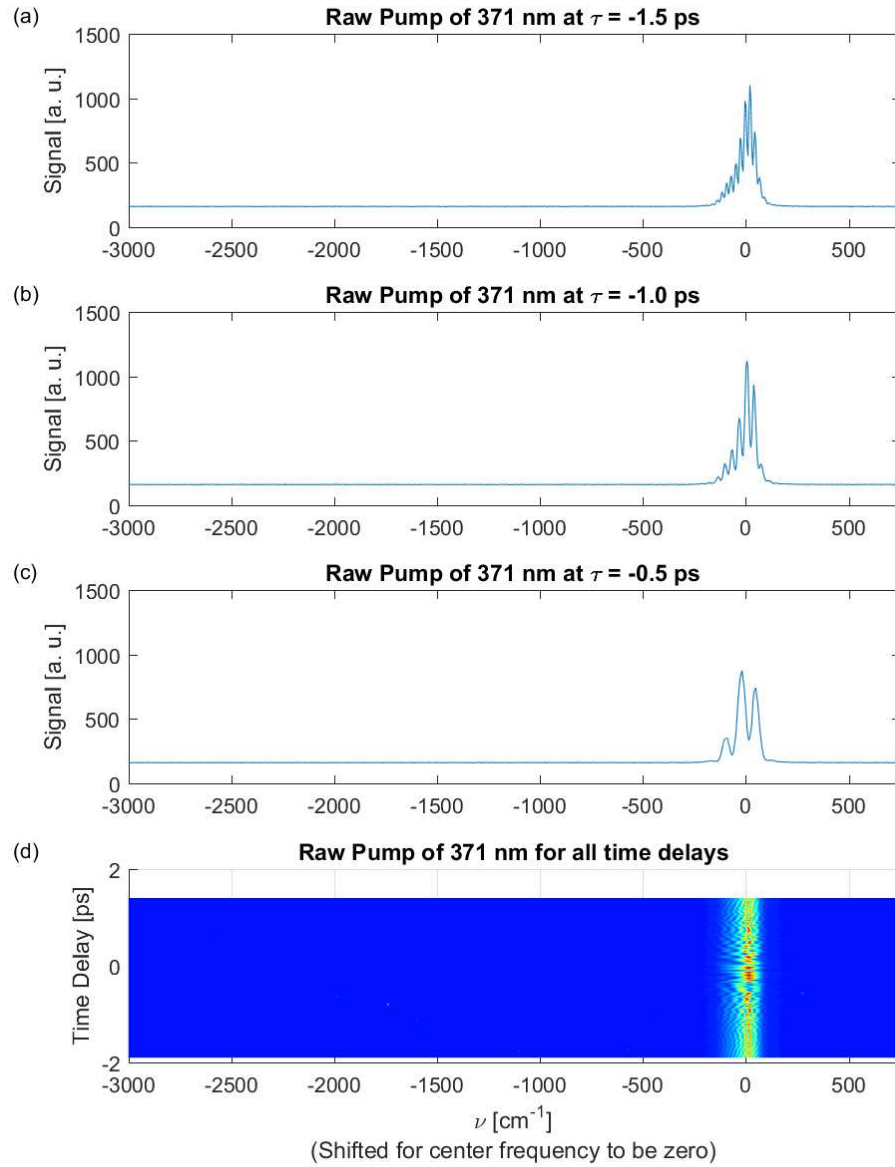


Figure 3.13: (a-c) Example of raw 371 nm pump spectra taken for various delay times. (d) Raw pump spectra for all recorded time delays. The left side of these spectra show the region over which the Stokes signal of interest would be, however this is filtered out, see Appendix A.

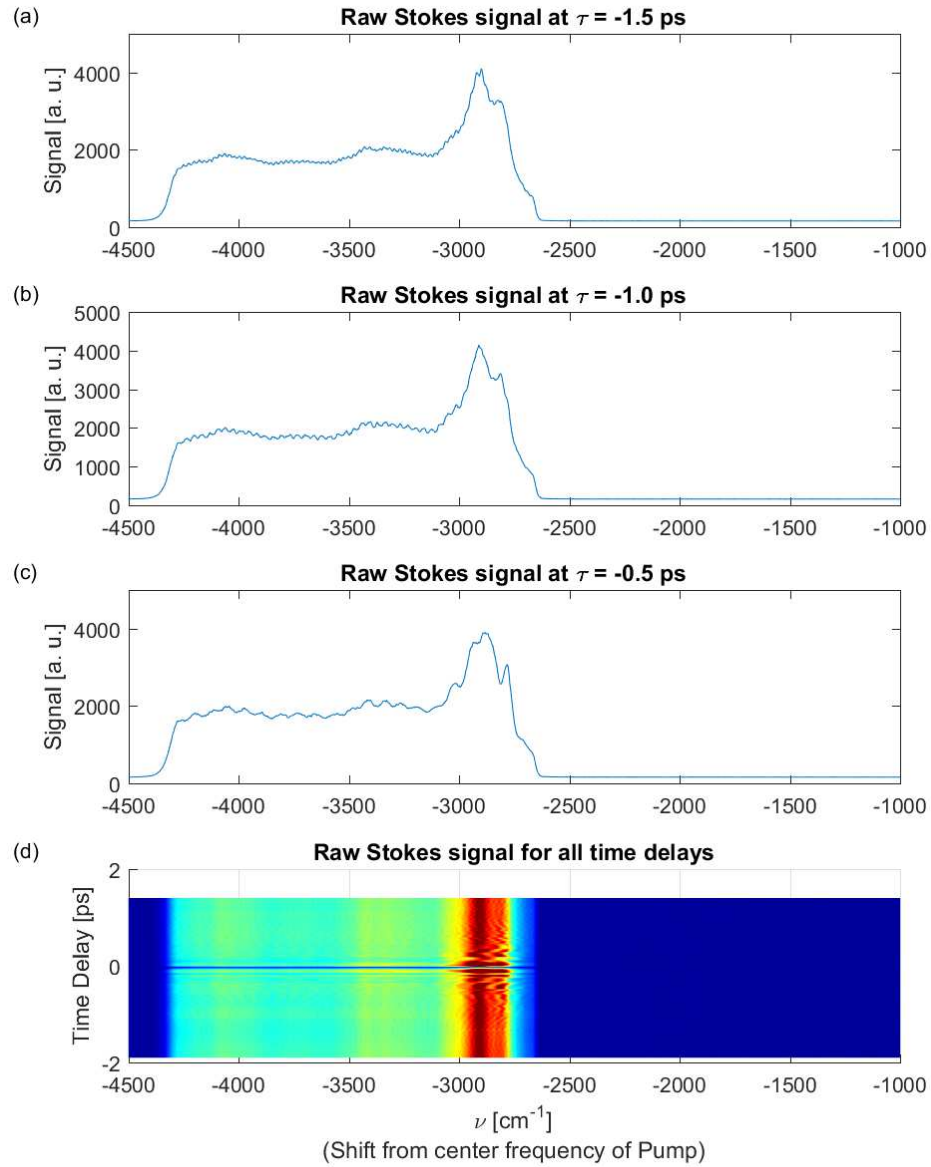


Figure 3.14: (a-c) Example of raw 2834 and 2944 cm $^{-1}$ Stokes spectrum taken taken for various delay times. (d) Raw Stokes spectra for all recorded time delays. The Stokes signal we expect here is propped up by a fluorescence background yet can still be readily seen.

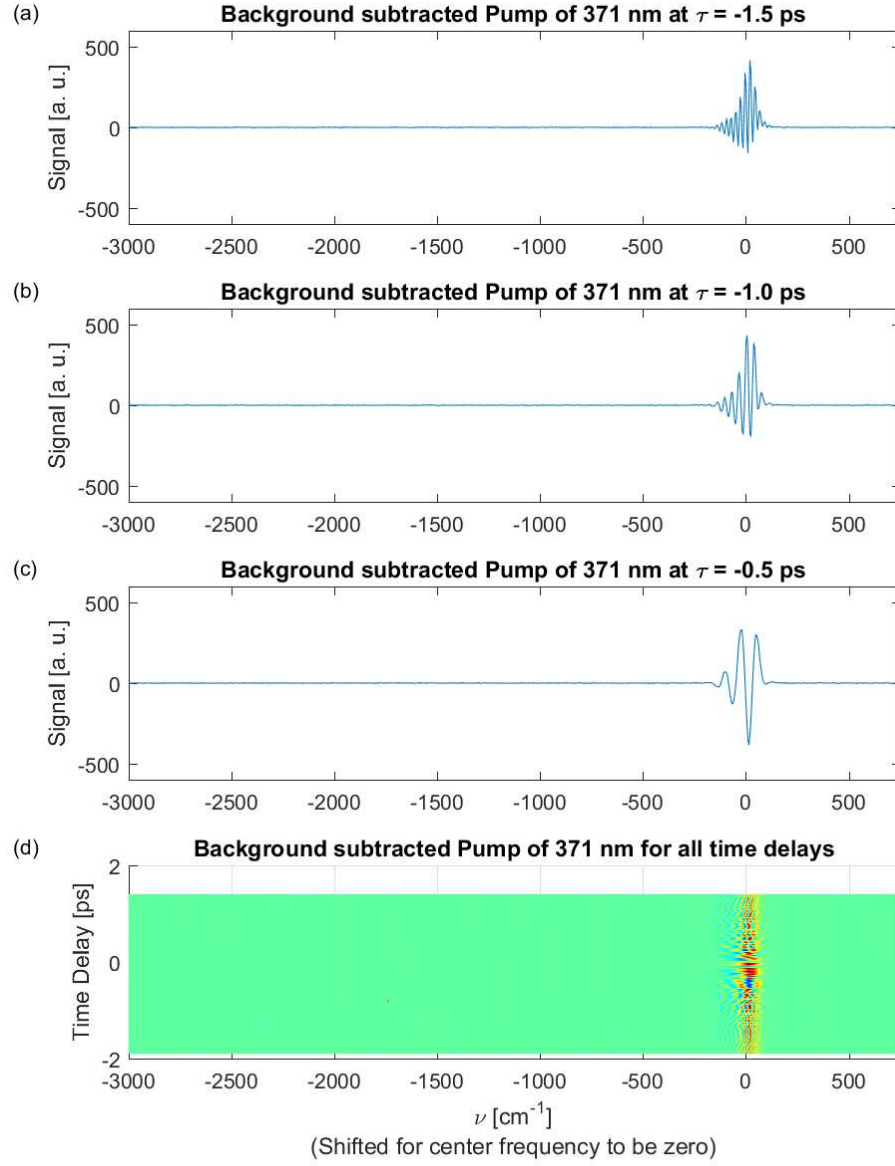


Figure 3.15: (a-c) Example of background subtracted 371 nm pump interference taken for various delay times. (d) Background subtracted pump spectra for all recorded time delays.

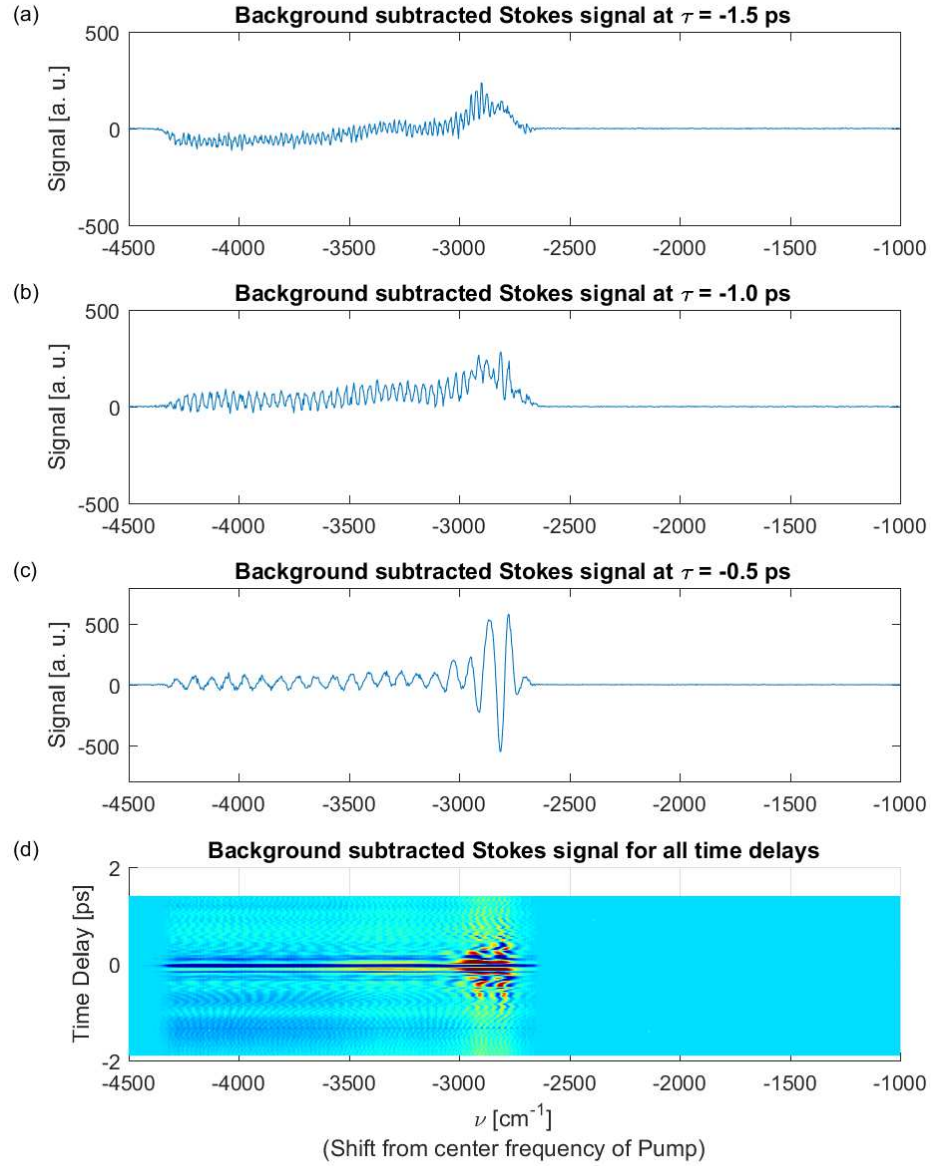


Figure 3.16: (a-c) Example of background subtracted 2834 and 2944 cm⁻¹ Stokes interference taken for various delay times. (c) Background subtracted Stokes spectra for all recorded time delays. The fluorescence shelf creates a long window (only limited by the filtering we chose) on which we can see the interference fringes caused by the time delay.

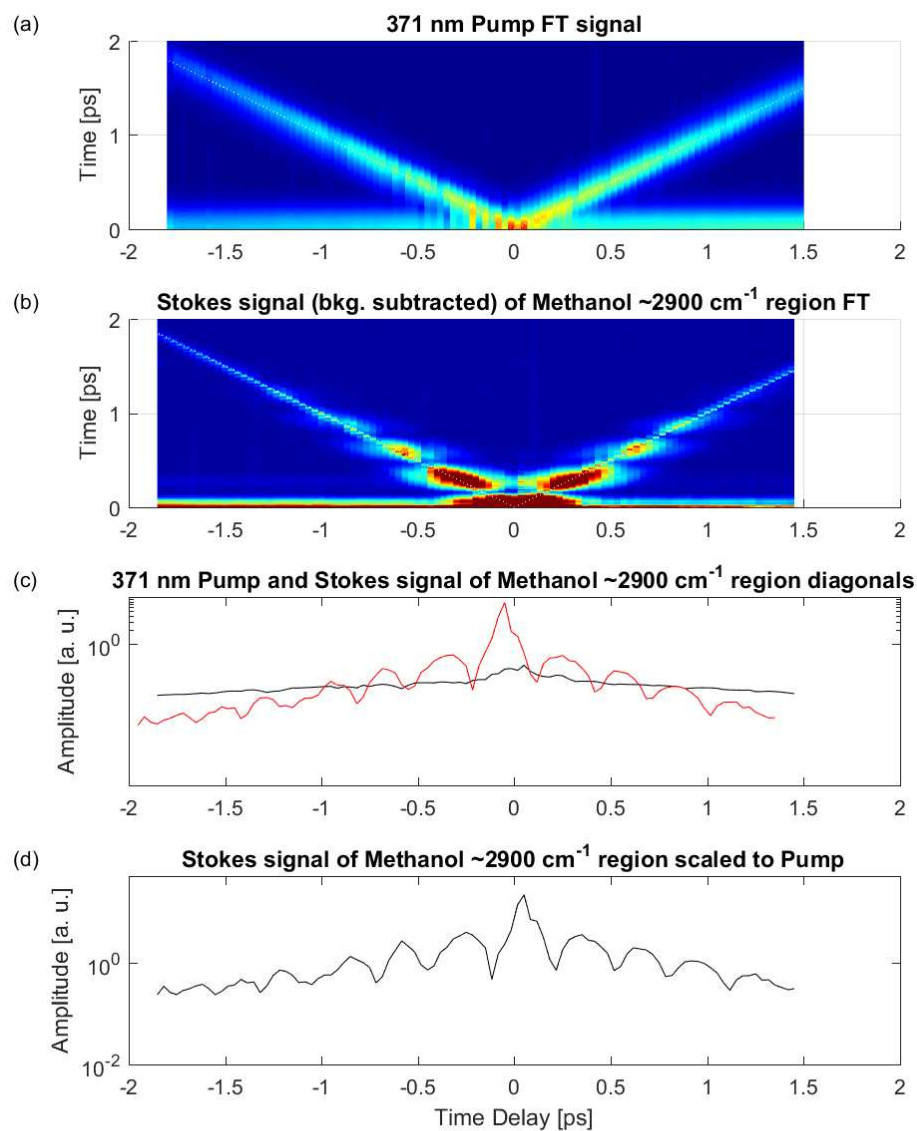


Figure 3.17: (a) Numerical Fourier Tranformed 371 nm pump signal. (b) Numerical Fourier Transformed 2834 and 2944 cm^{-1} Stokes signal. (c) Diagonals of pump and Stokes signal along the dashed lines. (d) Stokes signal scaled to pump.

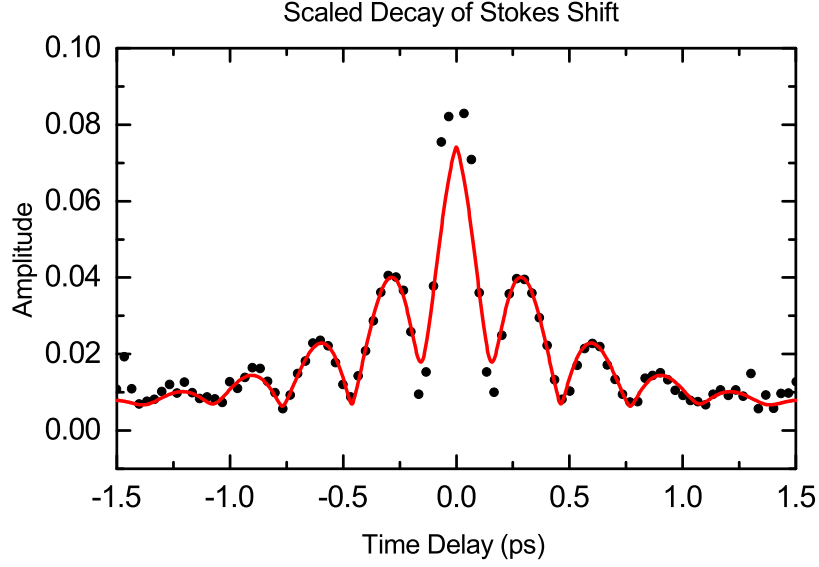


Figure 3.18: Scaled decay of 2834 and 2944 cm^{-1} stokes signals as a function of time delay between pulses. Data points representing the average of the Fourier Transformed Stokes signal from multiple data sets taken sequentially, all scaled by their recorded pump spectra. Solid curve is a numerical fitting using Eq. 2.19 for double modes, see Table 3.6.

Nonlinear fit for double mode 2834 and 2944 cm^{-1} in methanol

Reduced Chi-Sqr		8.95E-7
Adj. R-Square		0.98
Parameter	Value	
y_0	0.005	$\pm 5\text{E-}4$
A_1	0.022	± 0.002
A_2	0.047	± 0.003
$1/\Gamma_1$	0.67	± 0.089 ps
$1/\Gamma_2$	0.36	± 0.013 ps
$\Delta\nu_{21}$	108.41	± 0.25 cm^{-1}
$\Delta\phi_{21}$	0	Fixed
t_0	0	Fixed

Table 3.6: Nonlinear fit parameters for 2834 and 2944 cm^{-1} using Eq. 2.19, where we've added vertical and horizontal offsets y_0 and t_0 , and changed variables where $2\pi\nu_i = \omega_i$. The lifetimes and frequency splitting agrees with CW linewidth measurements and previously reported values [12].

Once again we scale the Stokes signal by the laser signal diagonals in Fig. 3.17.c to remove the resolution bias in the spectrometer. In Fig. 3.17.d we see the coherence beating between the two modes as a regular oscillation on top of the exponentially decaying coherence signal. By fitting this in Fig. 3.18, while again ignoring the points closet to zero delay time, with the expected Eq. 2.19 we find the lifetimes and difference frequency between the two modes shown in Table 3.6, agrees well with previously reported transient CARS measurements and other CW linewidth measurements [12].

3.3 Triple Resonance - Propanol

The TCUPS spectrum shown in Fig. 3.20 for a triple mode system in 2-propanol, $\sim 2900 \text{ cm}^{-1}$ shifts, was recorded with the laser pulse centered at 790 nm, and was frequency doubled to 385 nm. The filters used for this collection can be found in Appendix A. Preliminary collection of the spectra for this triple mode system showed delay time step sizes of $\sim 33 \text{ fs}$ might not be refined enough, so the step size for this data is reduced by half to $\sim 16.67 \text{ fs}$.

In Fig. 3.19.a-c we see that the interference of the pump is not perfect, as the fringes do not go to zero. This is due to the misalignment of the pump through the interferometer, which due to time constraints was not improved. We correct for this in the analysis when we divide the Stokes signal by the corresponding laser signal, but the lower visibility reduces our signal-to-noise ratio, as can be seen in Fig. 3.22. Even with this low signal-to-noise ratio we can distinguish the interference fringes. There is a fluorescent background that gives the spectrum a slight slant. This does not influence the analytical treatment and result. We were also able to record signal for $\sim 1400 - 1500 \text{ cm}^{-1}$ corresponding to twisting and wagging of the methyl groups; however, this was at the edge of our filtering so we could not explore these vibrational features further.

Fig. 3.21.a-c shows the background-subtracted laser signal for various delay times, and Fig. 3.21.d shows this signal for all delay times for a single data set. Similarly, Fig. 3.22.a-d shows the background-subtracted Stokes signal for these time delays.

It is evident in Fig. 3.22.a that the resolution of the spectrometer combined with low-visibility interference limit our ability to collect data for longer time delays. Again we take the Fourier transform of the laser and Stokes signals following the analysis detailed previously, as shown in Fig. 3.23.a-b. Although faint, Fig. 3.23.b shows a more complex coherence beating pattern than that is seen in the double mode data in methanol. The diagonals of the Fourier-transformed data sets, shown in Fig. 3.23.c, reveal the limitations due to spectral resolution in the laser signal, and the low signal-to-noise ratio due to poor visibility interference in the Stokes signal after ± 1.25 ps. The Stokes signal scaled by the laser is plotted in Fig. 3.23.d; the upward swing outside of ± 1.25 ps is due to the fact that the pump continues to show interference while the Stokes signal has vanished.

Finally in Fig. 3.24 we fit the resolution corrected signal to Eq. 2.19 using three modes, the results of which can be found in Table 3.7. Due to the near symmetry of the true four peak system, and even in the simplified three peak analysis, the fit algorithm ran into difficulty as the two outside modes had a tendency to swap values causing a run-away instability. Thus, amplitudes are held fixed, at values that approximate the relative integrated intensities of the modes, during the fitting procedure to allow for greater stability.

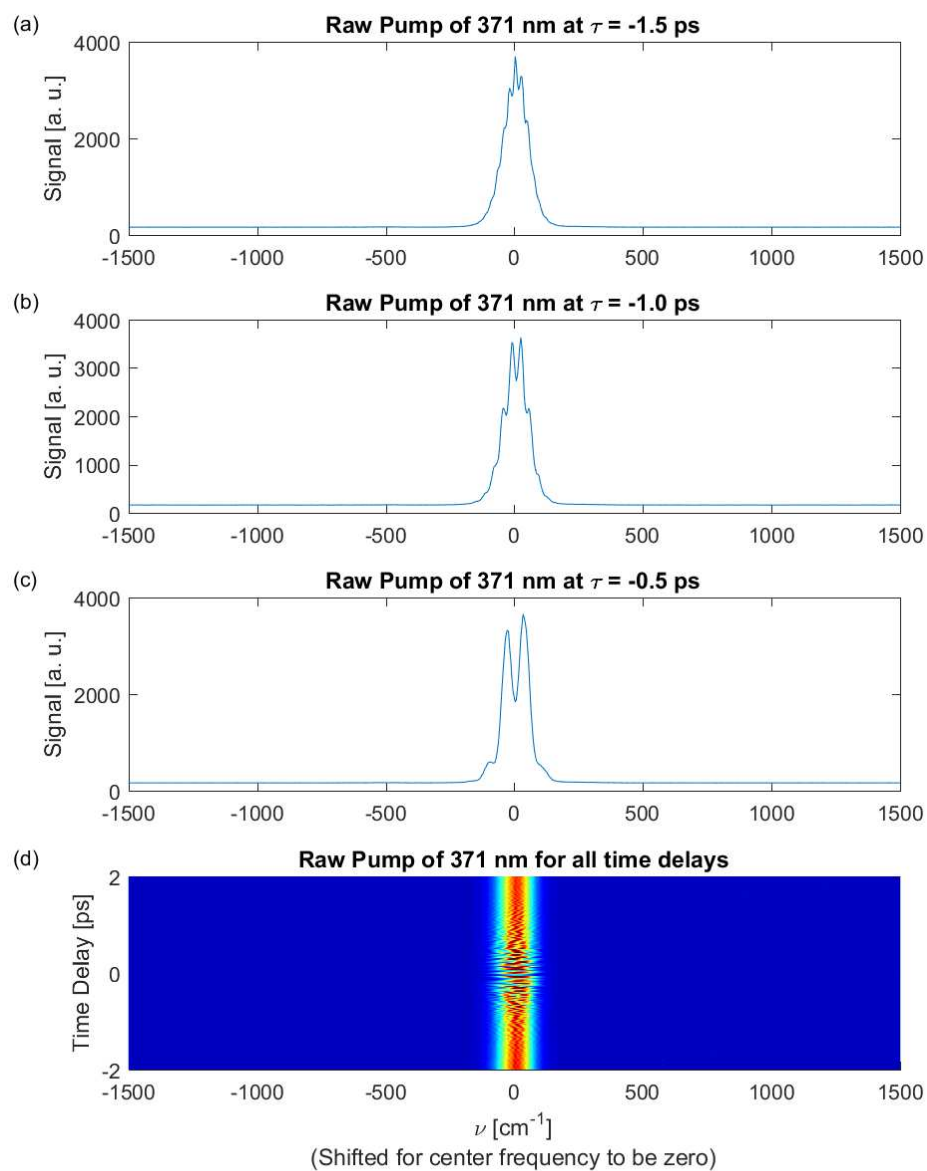


Figure 3.19: (a-c) Example of raw 385 nm pump spectra taken for various delay times. (d) Raw pump spectra for all recorded time delays. Filters used for this collection can be found in Appendix A.

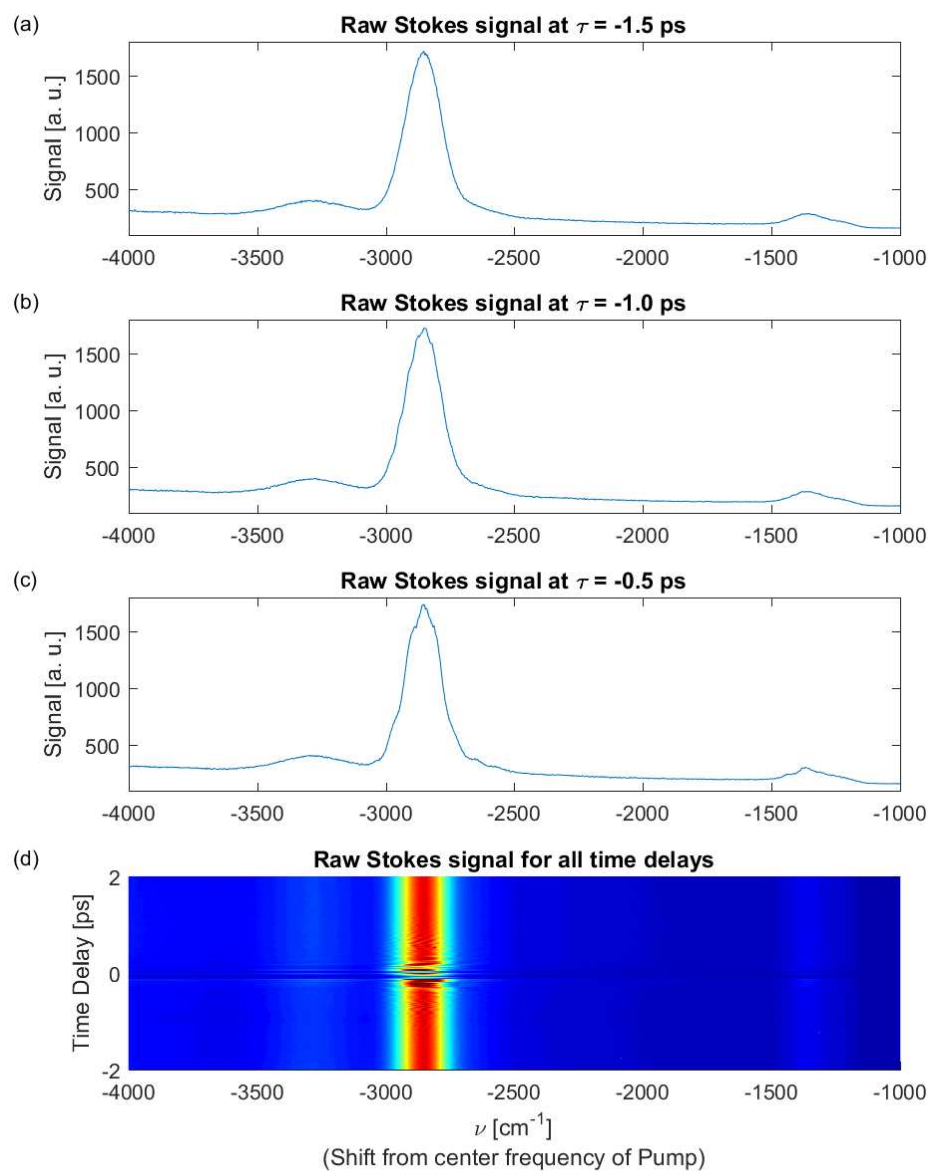


Figure 3.20: (a-c) Example of raw 2884, 2924, and 2976 cm⁻¹ Stokes spectra taken for various delay times. (d) Raw Stokes spectra for all recorded time delays.

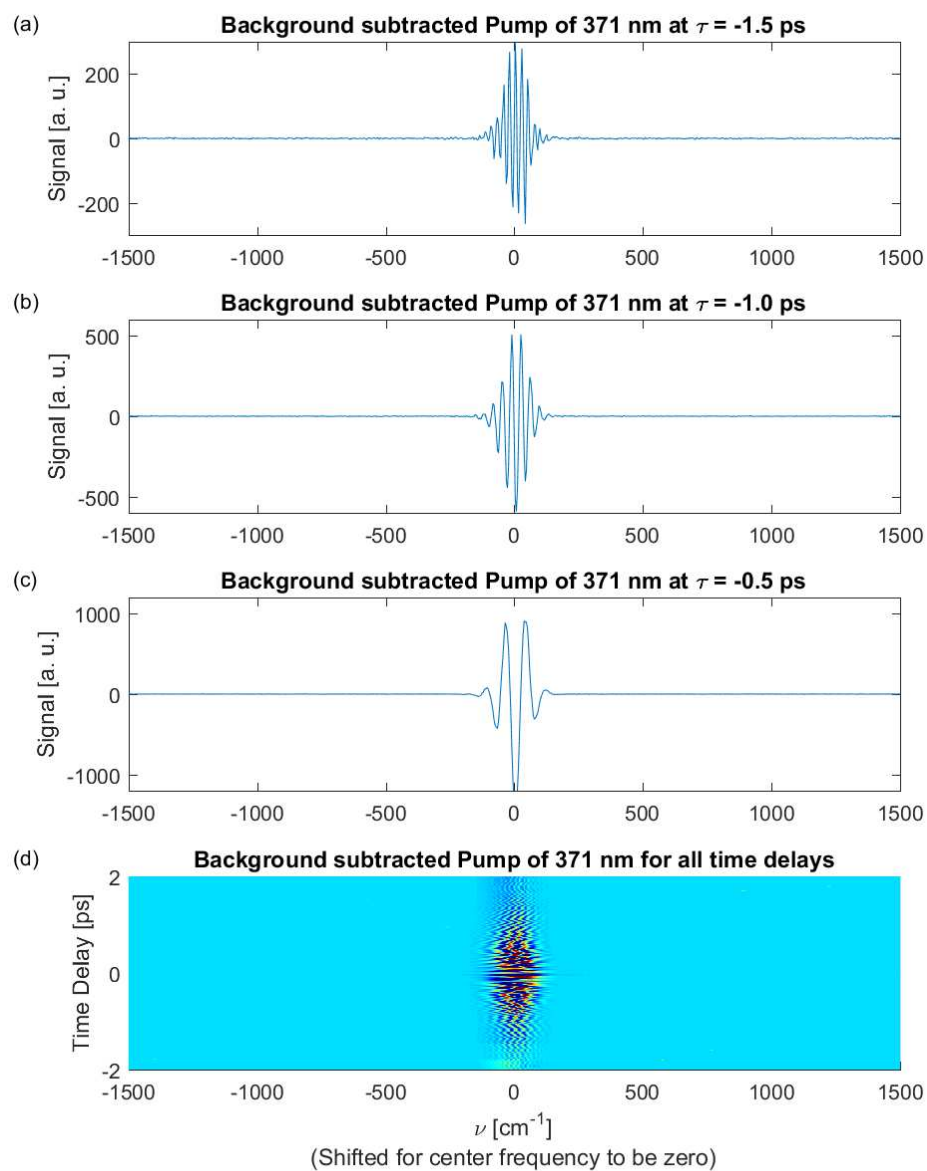


Figure 3.21: (a-c) Example of background subtracted 385 nm pump interference taken for various delay times. (d) Background subtracted pump spectra for all recorded time delays.

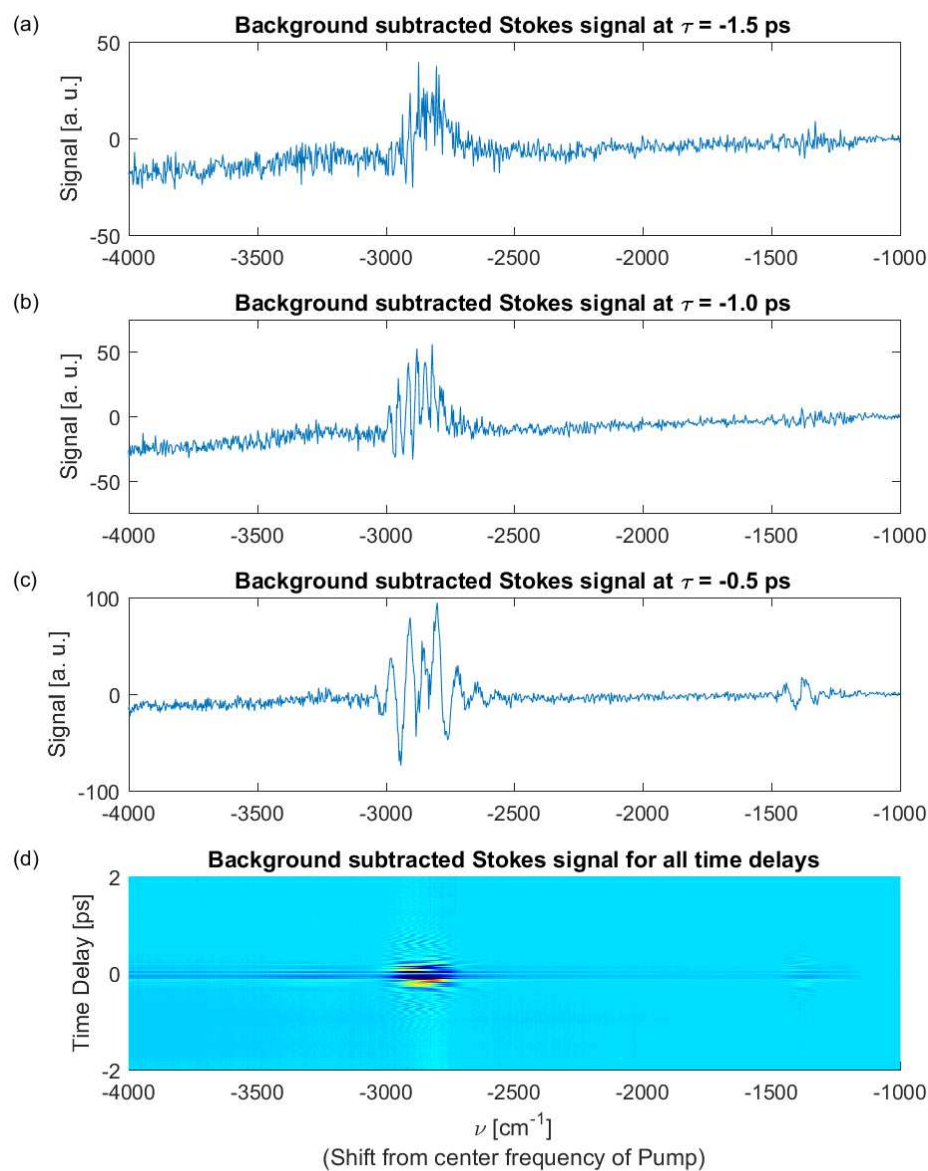


Figure 3.22: (a-c) Example of background subtracted 2884, 2924, and 2976 cm^{-1} Stokes interference taken for various delay times. (d) Background subtracted Stokes spectra for all recorded time delays.

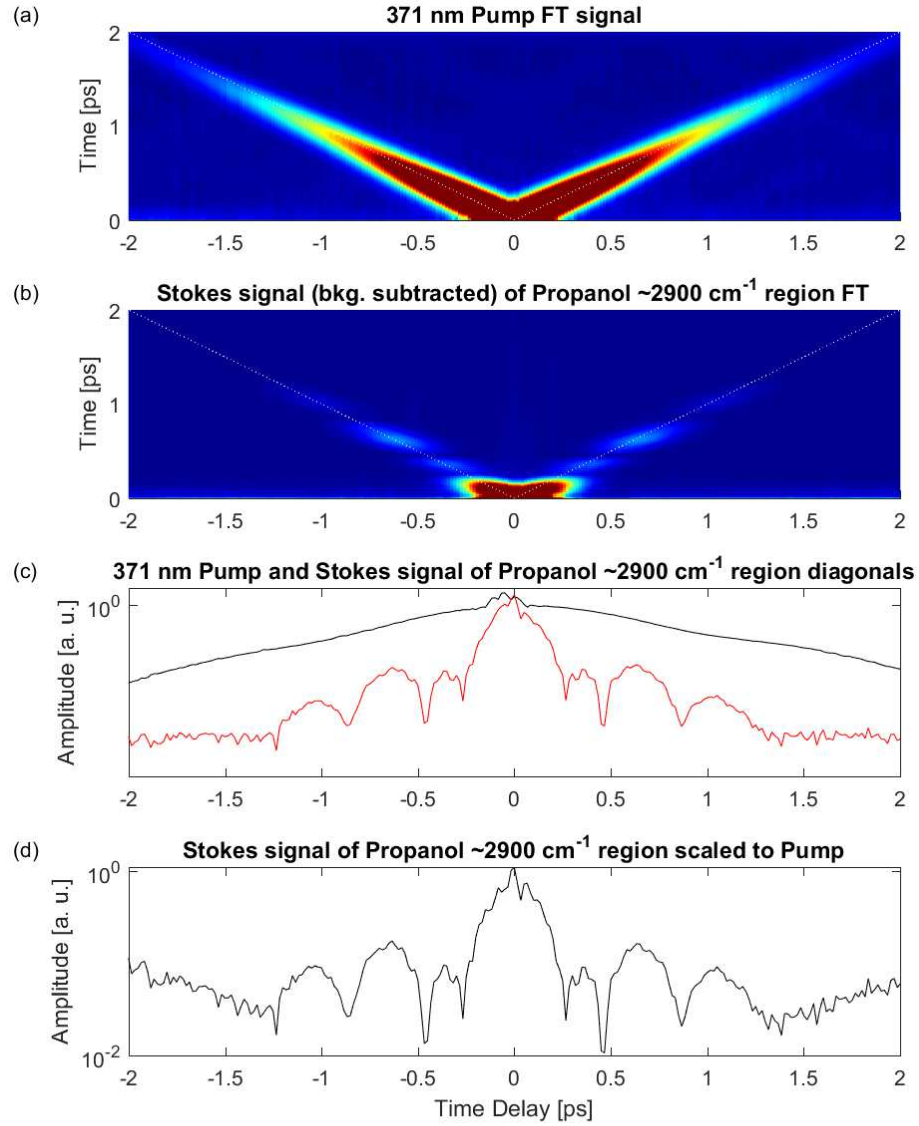


Figure 3.23: (a) Numerical Fourier Tranformed 385 nm pump signal. (b) Numerical Fourier Transformed 2884, 2924, and 2976 cm^{-1} Stokes signal. Dashed lines correspond to delay time $\tau = t$ the Fourier transform time coordinate. (c) Diagonals of pump and Stokes signal along the dashed lines. (d) Stokes signal scaled to pump.

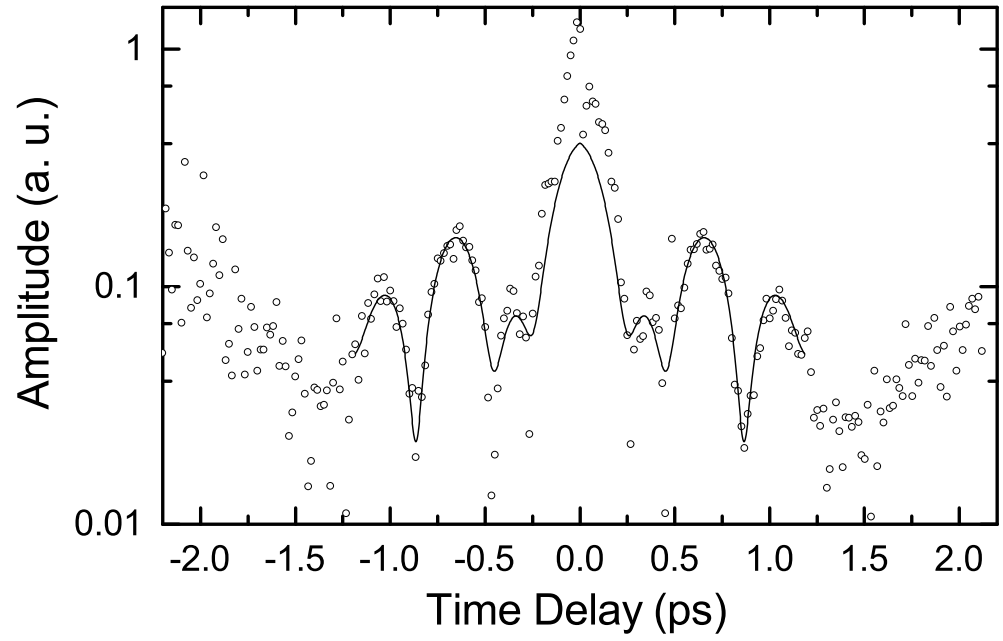


Figure 3.24: Scaled decay of 2884, 2924, and 2976 cm^{-1} Stokes signals as a function of time delay between pulses. Data points representing the average of the Fourier Transformed Stokes signal from multiple data sets taken sequentially, all scaled by their recorded pump spectra. Solid curve is a numerical fitting using Eq. 2.19 for triple modes, see Table 3.7.

Nonlinear fit for triple mode 2884, 2924, and 2976 cm^{-1} in 2-propanol

	Reduced Chi-Sqr	0.00114
	Adj. R-Square	0.22194
Parameter	Value	
y_0	-0.02	Fixed
A_1	0.09	Fixed
A_2	0.20	Fixed
A_3	0.13	Fixed
$1/\Gamma_1$	1.19	± 0.11 ps
$1/\Gamma_2$	0.69	± 0.05 ps
$1/\Gamma_3$	1.44	± 0.20 ps
$\Delta\nu_{21}$	36.16	± 0.65 cm^{-1}
$\Delta\nu_{31}$	98.22	± 0.49 cm^{-1}
$\Delta\nu_{32}$	54.73	± 0.45 cm^{-1}
$\Delta\phi_{21}$	0	Fixed
t_0	0	Fixed

Table 3.7: Nonlinear fit parameters for 2884, 2924, and 2976 cm^{-1} using Eq. 2.19, where we've added vertical and horizontal offsets y_0 and t_0 , and changed variables where $2\pi\nu_i = \omega_i$. The lifetimes and frequency splitting agree with CW linewidth measurements.

Chapter 4

DISCUSSION

Applying the TCUPS scheme allowed us to perform a spontaneous single-excitation-level measurement of molecular vibrations. Due to the spontaneous nature of the Raman signal generated through the TCUPS scheme, all possible vibrational modes are accessible, in contrast in CARS spectroscopy where the bandwidth of the stimulating laser field limits the frequency range of excitations that can be probed.

By selecting a single mode at 1033 cm^{-1} in methanol, and through the use of spectral filtering, we were able to measure the exponential decay of the coherence of a single mode and found for this specific mode that the measured lifetime agrees with CW linewidth measurements. The measurement was made in the red where the spectrometer issue of etaloning was clearly stronger than the signal we were looking for; however, the Fourier analysis of the signal removes this problem. Even with this large background TCUPS is effective in measuring the lifetime of interest.

Then by spectrally selecting a double mode at 2834 and 2944 cm^{-1} in methanol we recover coherence beating between these nearby modes. We thus expand the application of TCUPS to more than one mode. Because of this, we can not only measure the individual mode lifetimes but also find the difference frequency of the two modes. For the measurement we moved the center frequency into the blue where the system generates fluorescence. The background fluorescence is removable from the acquired Raman signal via the Fourier analysis.

Finally we looked at a more complicated triple mode at 2884 , 2924 , and 2976 cm^{-1} in 2-propanol. Again we recover the vibrational mode lifetimes and difference frequency, however the fit result contained fixed parameters. Here, spectrometer etaloning

wasn't very prevalent, nor was fluorescence. From the laser spectrum data we can observe that the spectral interference was not ideal, and furthermore, the amplitude of the Stokes interference has low visibility. Even under these less than ideal recording conditions, the Fourier analysis is still able to extract the information of the mode lifetimes and difference frequencies with minimal signal-to-noise ratio, but the range of delays with good signal-to-noise is not enough to obtain a fit with free amplitude parameters.

Another aspect to consider for this particular case is the true Raman response in this region. We've used a three mode analysis, but this may not be the best as there are truly four modes of comparable amplitude [65]. Finer time-step and spectrometer resolutions would be necessary to be able to analyze this region using four modes. Additionally, we should address the symmetry of this region in 2-propanol. As seen in Table 3.3, the difference between the center of the modes Peak1 and Peak2 is roughly the same as that of modes Peak3 and Peak4. The similar beat frequencies may interfere, which is not accounted for in our analysis; this is a potential topic for further investigation.

Along these lines, we should also revisit the other two systems. For the "single" mode investigated at 1033 cm^{-1} there exists a weaker Raman peak around 1113 cm^{-1} . A question arises about how this influences the signal we've measured. Initially we only applied a fit with one mode. Because of the large difference in the amplitudes and the already present issues with etaloning and signal-to-noise, it is not possible with the data set here to extract more than the single mode lifetime.

In the "double" resonance case there isn't the symmetry like that in the "triple" mode analysis, but we can see in Fig. 3.5 that there are at least three modes of comparable integrated intensity and an extra smaller shoulder close to 3000 cm^{-1} , see Table 3.2 for more information. Again the limited signal-to-noise ratio, and number and spacing of time delays taken prevent us from a full multi-mode analysis. So at the moment this is left as an open problem to consider in the future.

4.1 Future Goals for TCUPS

TCUPS can measure the relative phase between vibrational modes, as shown in ϕ_i of Eq. 2.10. Phase-stabilization of the interferometer would allow exploration of this capability, which is outside the capability range of the CARS scheme.

The addition of polarization of the laser field and participating modes as an extra degree of freedom [54, 65], may allow for measurement of thermal motions, such as rotation of the molecular sample as the time delay between pump and probe is increased.

4.2 Conclusion

The alcohols studied here are complex molecules that contain a variety of vibrational resonances. The Raman response spectrum of the alcohols present numerous opportunities for interesting testing grounds for TCUPS. In methanol we were able to study an isolated (or nearly so) vibrational mode in analogy to that explored in the initial experiment in solid-state-diamond. By applying Fourier analysis, we were able to overcome signal degradation due to detector artifacts. Measurement of the double mode in methanol extends the TCUPS technique to multiple modes. In this case we recovered the coherence oscillation signal reported in previous CARS experiments, and found lifetimes that agree with other methods of measurement. Lastly we measured a system in 2-propanol that presented three (or truly four) modes, which applied TCUPS to the measurement of systems with more than two modes.

Even with signal degradation cause by detector issues, expression of strong fluorescence, or simply low signal-to-noise ratio, the Transient Coherent Ultrafast Phonon Spectroscopy scheme and the analysis developed for it still finds the signal of interest, demonstrating that TCUPS is a robust technique for molecular vibrational spectroscopy.

BIBLIOGRAPHY

- [1] C. V. Raman. A new radiation*. *Indian J. Phys.*, 2:387–398, 1928.
- [2] A. Smekal. Zur quantentheorie der dispersion. *Naturwissenschaften*, 11(43):873–875, 1923.
- [3] G .S. Landsberg and L. I. Mandelstam. New phenomenon in scattering of light (preliminary report). *Journal of the Russian Physico-Chemical Society, Physics Section*, 60:335, 1928.
- [4] S. Mukamel. *Principles of Nonlinear Optical Spectroscopy*. Oxford University Press, 1995.
- [5] R. W. Boyd. *Nonlinear Optics*. Academic Press, 3 edition, 2008.
- [6] I. V. Hertel and W. Radloff. Ultrafast dynamics in isolated molecules and molecular clusters. *Reports on Progress in Physics*, 69(6):1897, 2006.
- [7] K. Wolfrum, H. Graener, and A. Laubereau. Sum-frequency vibrational spectroscopy at the liquidair interface of methanol. water solutions. *Chemical Physics Letters*, 213(1):41 – 46, 1993.
- [8] M. Matsumoto and K. E. Gubbins. Hydrogen bonding in liquid methanol. *The Journal of Chemical Physics*, 93(3):1981–1994, 1990.
- [9] R. Laenen, G. M. Gale, and N. Lascoux. Ir spectroscopy of hydrogen-bonded methanol: Vibrational and structural relaxation on the femtosecond time scale. *The Journal of Physical Chemistry A*, 103(50):10708–10712, 1999.
- [10] G. Garberoglio and R. Vallauri. Instantaneous normal mode analysis of liquid methanol. *The Journal of Chemical Physics*, 115(1):395–401, 2001.
- [11] P. Jedlovsky. The local structure of various hydrogen bonded liquids: Voronoi polyhedra analysis of water, methanol, and hf. *The Journal of Chemical Physics*, 113(20):9113–9121, 2000.
- [12] D. Pestov, M. Zhi, Z. Sariyanni, N. G. Kalugin, A. Kolomenskii, R. Murawski, Y. V. Rostovtsev, V. A. Sautenkov, A.V. Sokolov, and M. O. Scully. Femtosecond cars of methanolwater mixtures. *Journal of Raman Spectroscopy*, 37(1-3):392–396, 2006.

- [13] Y. Numata, Y. Iida, and H. Tanaka. Quantitative analysis of alcoholwater binary solutions using raman spectroscopy. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 112(6):1043 – 1049, 2011.
- [14] J.-H. Guo, Y. Luo, A. Augustsson, S. Kashtanov, J.-E. Rubensson, D. K. Shuh, H. Ågren, and J. Nordgren. Molecular structure of alcohol-water mixtures. *Phys. Rev. Lett.*, 91:157401, Oct 2003.
- [15] Y. Sun, R. Zheng, and Q. Shi. Theoretical study of raman spectra of methanol in aqueous solutions: Non-coincident effect of the co stretch. *The Journal of Physical Chemistry B*, 116(15):4543–4551, 2012.
- [16] S. P. S. Porto. Angular dependence and depolarization ratio of the raman effect. *J. Opt. Soc. Am.*, 56(11):1585–1586, Nov 1966.
- [17] A. Laubereau and W. Kaiser. Vibrational dynamics of liquids and solids investigated by picosecond light pulses. *Rev. Mod. Phys.*, 50:607–665, Jul 1978.
- [18] M. G. Raymer and J. Mostowski. Stimulated raman scattering: Unified treatment of spontaneous initiation and spatial propagation. *Phys. Rev. A*, 24:1980–1993, Oct 1981.
- [19] S. Mukamel, A. Piryatinski, and V. Chernyak. Two-dimensional raman echoes: femtosecond view of molecular structure and vibrational coherence. *Accounts Chem. Res.*, 32:145154, 1999.
- [20] S. Mukamel. Multidimensional femtosecond correlation spectroscopies of electronic and vibrational excitations. *Annual Review of Physical Chemistry*, 51(1):691–729, 2000.
- [21] B. Dunlap, P. Richter, and D. W. McCamant. Stimulated raman spectroscopy using chirped pulses. *Journal of Raman Spectroscopy*, 45(10):918–929, 2014.
- [22] J. C. Schaefer and I. Chabay. Generation of enhanced coherent anti-stokes raman spectroscopy signals in liquid-filled waveguides. *Opt. Lett.*, 4(8):227–229, Aug 1979.
- [23] R. Altkorn, I. Koev, and M. J. Pelletier. Raman performance characteristics of teflon®-af 2400 liquid-core optical-fiber sample cells. *Appl. Spectrosc.*, 53(10):1169–1176, Oct 1999.
- [24] J. Scholl. Liquid-core waveguide for enhanced laser raman spectroscopy in oceanic applications. Technical report, Monterey Bay Aquarium Research Institute, 2006. An optional note.
- [25] F. M. Kamga and M. G. Sceats. Pulse-sequenced coherent anti-stokes raman scattering spectroscopy: a method for suppression of the nonresonant background. *Opt. Lett.*, 5(3):126–128, Mar 1980.

- [26] M. A. Yuratch. Effects of laser linewidth on coherent antiStokes Raman-spectroscopy. *Molecular Physics*, 38(2):625–655, 1979.
- [27] M. Schmitt, G. Knopp, A. Materny, and W. Kiefer. Femtosecond time-resolved coherent anti-stokes raman scattering for the simultaneous study of ultrafast ground and excited state dynamics: iodine vapour. *Chemical Physics Letters*, 270(12):9 – 15, 1997.
- [28] Y. Silberberg. Quantum coherent control for nonlinear spectroscopy and microscopy. *Annual Review of Physical Chemistry*, 60(1):277–292, 2009.
- [29] H. U. Stauffer, J. D. Miller, M. N. Slipchenko, T. R. Meyer, B. D. Prince, S. Roy, and J. R. Gord. Time- and frequency-dependent model of time-resolved coherent anti-stokes raman scattering (cars) with a picosecond-duration probe pulse. *The Journal of Chemical Physics*, 140(2), 2014.
- [30] A. Zumbusch, G. R. Holtom, and X. S. Xie. Three-dimensional vibrational imaging by coherent anti-stokes raman scattering. *Phys. Rev. Lett.*, 82:4142–4145, May 1999.
- [31] A. Volkmer, J.-X. Cheng, and X. S. Xie. Vibrational imaging with high sensitivity via epidetected coherent anti-stokes raman scattering microscopy. *Phys. Rev. Lett.*, 87:023901, Jun 2001.
- [32] J.-X. Cheng, A. Volkmer, and X. S. Xie. Theoretical and experimental characterization of coherent anti-stokes raman scattering microscopy. *J. Opt. Soc. Am. B*, 19(6):1363–1375, Jun 2002.
- [33] K. P. Knutsen, J. C. Johnson, A. E. Miller, P. B. Petersen, and R. J. Saykally. High spectral resolution multiplex {CARS} spectroscopy using chirped pulses. *Chemical Physics Letters*, 387(46):436 – 441, 2004.
- [34] N. Belabas and D. M. Jonas. Three-dimensional view of signal propagation in femtosecond four-wave mixing with application to the boxcars geometry. *J. Opt. Soc. Am. B*, 22(3):655–674, Mar 2005.
- [35] F. C. Waldermann, Benjamin J. Sussman, J. Nunn, V. O. Lorenz, K. C. Lee, K. Surmacz, K. H. Lee, D. Jaksch, I. A. Walmsley, P. Spizziri, P. Olivero, and S. Praver. Measuring phonon dephasing with ultrafast pulses using raman spectral interference. *Phys. Rev. B*, 78:155201, Oct 2008.
- [36] T. Shimanouchi. Tables of molecular vibrational frequencies: Consolidated volume i. *US Department of Commerce, National Bureau of Standards, Washington, DC*, 1972.
- [37] E. B. Wilson Jr., J. C. Decius, and P. C. Cross. *Molecular Vibrations*. Dover, 1980.

- [38] L. A. Woodward. *Introduction to the Theory of Molecular Vibrations and Vibrational Spectroscopy*. Oxford University press, 1972.
- [39] M. Diem. *Introduction to Modern Vibrational Spectroscopy*. John Wiley & Sons, 1993.
- [40] M. D. Fayer. *Ultrafast infrared and Raman spectroscopy*. New York: Marcel Dekker, 2001.
- [41] R. L. McCreery. *Photometric Standards for Raman Spectroscopy*. John Wiley & Sons, 2002.
- [42] P. J. Larkin. *IR and Raman Spectroscopy*. Elsevier, 2011.
- [43] K. Kwac and E. Geva. Mixed quantum-classical molecular dynamics study of the hydroxyl stretch in methanol/carbon-tetrachloride mixtures ii: Excited state hydrogen bonding structure and dynamics, infrared emission spectrum, and excited state lifetime. *The Journal of Physical Chemistry B*, 116(9):2856–2866, 2012.
- [44] K. Kwac and E. Geva. A mixed quantum-classical molecular dynamics study of the hydroxyl stretch in methanol/carbon tetrachloride mixtures iii: Nonequilibrium hydrogen-bond dynamics and infrared pumpprobe spectra. *The Journal of Physical Chemistry B*, 117(25):7737–7749, 2013.
- [45] W. L. Jorgensen. Structure and properties of liquid methanol. *J. Am. Chem. Soc.*, pages 543–549, 1 1980.
- [46] A. Fendt, S. F. Fischer, and W. Kaiser. Vibrational lifetime and Fermi resonance in polyatomic molecules. *Chemical Physics*, 57:55–64, May 1981.
- [47] Hajime Torii and Mitsuo Tasumi. Local order and transition dipole coupling in liquid methanol and acetone as the origin of the raman noncoincidence effect. *The Journal of Chemical Physics*, 99(11):8459–8465, 1993.
- [48] J. E. Bertie, S. L. Zhang, and C. D. Keefe. Measurement and use of absolute infrared absorption intensities of neat liquids. *Vibrational Spectroscopy*, 8(2):215 – 229, 1995. 6th Austrian-Hungarian International Conference on Vibrational Spectroscopy.
- [49] R. Chelli, S. Ciabatti, G. Cardini, R. Righini, and P. Procacci. Calculation of optical spectra in liquid methanol using molecular dynamics and the chemical potential equalization method. *The Journal of Chemical Physics*, 111(9):4218–4229, 1999.
- [50] U. Buck and F. Huisken. Infrared spectroscopy of size-selected water and methanol clusters. *Chemical Reviews*, 100(11):3863–3890, 2000.

- [51] L. K. Iwaki and D. D. Dlott. Ultrafast vibrational energy redistribution within ch and oh stretching modes of liquid methanol. *Chemical Physics Letters*, 321(56):419 – 425, 2000.
- [52] L. K. Iwaki and D. D. Dlott. Three-dimensional spectroscopy of vibrational energy relaxation in liquid methanol. *The Journal of Physical Chemistry A*, 104(40):9101–9112, 2000.
- [53] Tolga S. Gulmen and Edwin L. Sibert. Vibrational energy relaxation of the oh(d) stretch fundamental of methanol in carbon tetrachloride. *The Journal of Chemical Physics*, 123(20):–, 2005.
- [54] Y. Yu, Y. Wang, K. Lin, N. Hu, X. Zhou, and S. Liu. Complete raman spectral assignment of methanol in the ch stretching region. *The Journal of Physical Chemistry A*, 117(21):4377–4384, 2013. PMID: 23639010.
- [55] E. K. Plyer. Infrared spectra of methanol, ethanol, and n-propanol. *J. Res. Bur. Standards*, 48(4):281, 1952.
- [56] U. Liddel and E. D. Becker. Infra-red spectroscopic studies of hydrogen bonding in methanol, ethanol, and t-butanol. *Spectrochimica Acta*, 10(1):70 – 84, 1957.
- [57] J. H. S. Green. Thermodynamic properties of organic oxygen compounds. part 12.-vibrational assignment and calculated thermodynamic properties 0-1000[degree] k of isopropyl alcohol. *Trans. Faraday Soc.*, 59:1559–1563, 1963.
- [58] M. J. Colles and J. E. Griffiths. Relative and absolute raman scattering cross sections in liquids. *The Journal of Chemical Physics*, 56(7):3384–3391, 1972.
- [59] A. Laubereau, D. von der Linde, and W. Kaiser. Direct measurement of the vibrational lifetimes of molecules in liquids. *Phys. Rev. Lett.*, 28:1162–1165, May 1972.
- [60] H. H. Eysel and J. E. Bertie. Integrated ir and raman intensities of aliphatic alcohols in the liquid phase. *Journal of Molecular Structure*, 142:227 – 230, 2001.
- [61] N. A. Atamas, A. M. Yaremko, L. A. Bulavin, V. E. Pogorelov, S. Berski, Z. Latajka, H. Ratajczak, and A. Abkowicz-Bieko. Anharmonic interactions and fermi resonance in the vibrational spectra of alcohols. *Journal of Molecular Structure*, 605(23):187 – 198, 2002.
- [62] R. Lu, W. Gan, B. Wu, Z. Zhang, Y. Guo, and H. Wang. Ch stretching vibrations of methyl, methylene and methine groups at the vapor/alcohol (n = 18) interfaces. *The Journal of Physical Chemistry B*, 109(29):14118–14129, 2005.

- [63] P. He, H. L. Wang, R. W. Fan, D. Y. Chen, Y. Q. Xia, X. Yu, J. L. Wang, and Y. G. Jiang. Terahertz beats of vibrational modes in methanol and ethanol selectively excited by tr-cars technique. *Science China Physics, Mechanics and Astronomy*, 55(12):2351–2356, 2012.
- [64] M Holtz, PK Dasgupta, and GF Zhang. Small-volume raman spectroscopy with a liquid core waveguide. *Analytical Chemistry*, 71(14):2934–2938, JUL 15 1999.
- [65] Y. Yu, Y. Wang, N. Hu, K. Lin, X. Zhou, and S. Liu. Overlapping spectral features and new assignment of 2-propanol in the ch stretching region. *Journal of Raman Spectroscopy*, 45(3):259–265, 2014.
- [66] S. Meiselman, O. Cohen, M. F. DeCamp, and V. O. Lorenz. Measuring vibrational coherence lifetimes in liquid methanol using transient coherent raman scattering. *Journal of Physics: Conference Series*, 497(1):012004, 2014.
- [67] S. Meiselman, O. Cohen, M. F. DeCamp, and V. O. Lorenz. Observation of coherence oscillations of single ensemble excitations in methanol. *J. Opt. Soc. Am. B*, 31(9):2131–2135, Sep 2014.
- [68] S. Meiselman, M. F. DeCamp, and V. O. Lorenz. Ultrafast coherent spontaneous raman spectroscopy of 2-propanol. *in submission at time of thesis*, 2016.
- [69] K. C. Lee, B. J. Sussman, J. Nunn, V. O. Lorenz, K. Reim, D. Jaksch, I.A. Walmsley, P. Spizzirri, and S. Praver. Comparing phonon dephasing lifetimes in diamond using transient coherent ultrafast phonon spectroscopy. *Diamond and Related Materials*, 19(10):1289 – 1295, 2010.
- [70] E. Hecht. *Optics*. Addison-Wesley, 4 edition, 2001.
- [71] W. M. Tolles, J. W. Nibler, J. R. McDonald, and A. B. Harvey. A review of the theory and application of coherent anti-stokes raman spectroscopy (cars). *Applied Spectroscopy*, 31(4):253–271, 8 1977.

Appendix A

INTERFERENCE FILTERS

A large collection of interference filters were used throughout the experimentation in this thesis. Some only for testing which fundamental wavelengths to use, others for data recording, see Chapter 2.1. They were used for adjusting intensity, selecting specific frequency ranges, and separating the pump from the Stokes signal. In most cases, the filters shown here were used in combination for enhanced selectivity.

For convenience, the transmission spectra for the filters listed in Table A.1 are shown in Figs A.1, A.2 and A.3. A numerical example of the effect the filtering would have on the data collection process, as seen through counts on the spectrometer's CCD camera, is shown in Fig. A.4.

Fig. Graph	Semrock Serial	Center λ (nm)	Width (nm) or Type
A.1.a	FF01-390/40	390	40
A.1.b	FF01-395/11	395	11
A.1.c	FF01-405/150	405	150
A.1.d	FF02-409/LP	409	Long Pass
A.1.e	FF01-425/26	425	26
A.1.f	FF01-450/70	450	70
A.1.g	FF510-Di02	510	Dichroic
A.1.h	FF01-609/54	609	54
A.2.a	FF01-630/20	630	20
A.2.b	FF01-640/40	640	40
A.2.c	FF01-650/SP	650	Short Pass
A.2.d	FF660-Di02	660	Dichroic
A.2.e	FF685-Di02	685	Dichroic
A.2.f	FF01-710/40	710	40
A.2.g	FF01-769/41	769	41
A.2.h	FF01-775/SP	775	Short Pass
A.3.a	SP01-785RU	785	Short Pass
A.3.b	FF01-785/62	785	62
A.3.c	BLP01-785R	785	Long Pass
A.3.d	LPD01-785RS	785	Long Pass
A.3.e	NF03-785E	785	Notch
A.3.f	FF01-786/22	786	22
A.3.g	FF01-788/20	788	20
A.3.h	FF02-809/81	809	81
A.3.i	LP02-830R	830	Long Pass
A.3.j	FF01-832/37	832	37

Table A.1: Spectral filters from Semrock (see www.semrock.com). Transmission as a function of wavelength can be seen in [Fig. A.1](#), [Fig. A.3](#), and [Fig. A.3](#).

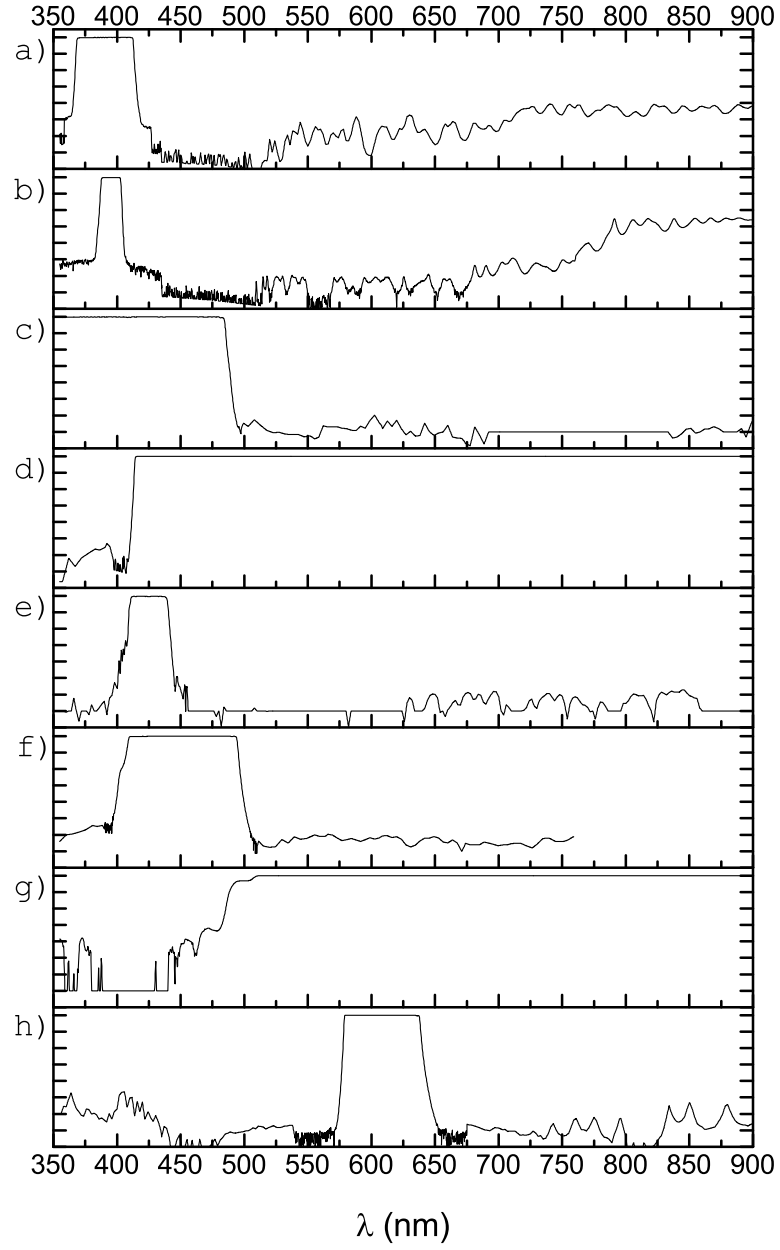


Figure A.1: Interference filter transmission spectra corresponding to Table A.1. Y-axis in OD (highest tick is OD-0, ticks below go as OD-1, OD-2, etc.). Plots here come from Semrock's average transmission data (see www.semrock.com).

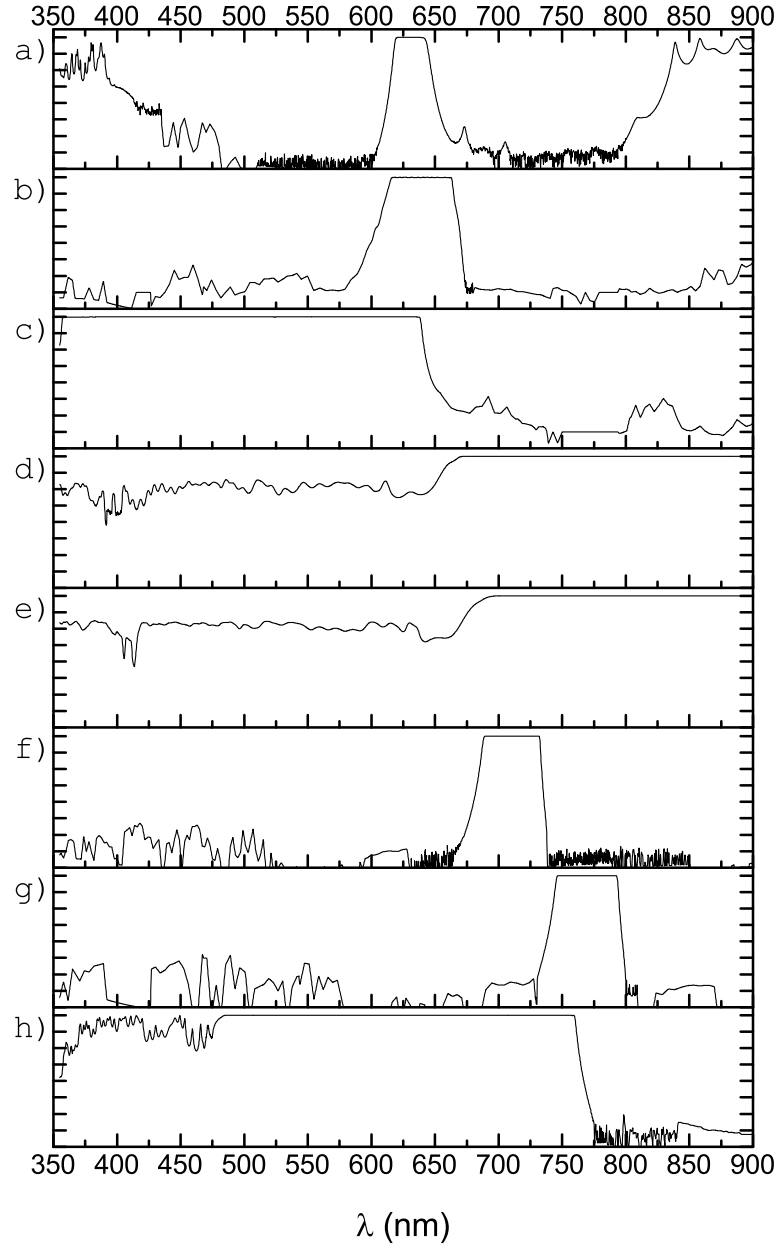


Figure A.2: Interference filter transmission spectra corresponding to Table A.1. Y-axis in in OD (highest tick is OD-0, ticks below go as OD-1, OD-2, etc.). Plots here come from Semrock's average transmission data (see www.semrock.com).

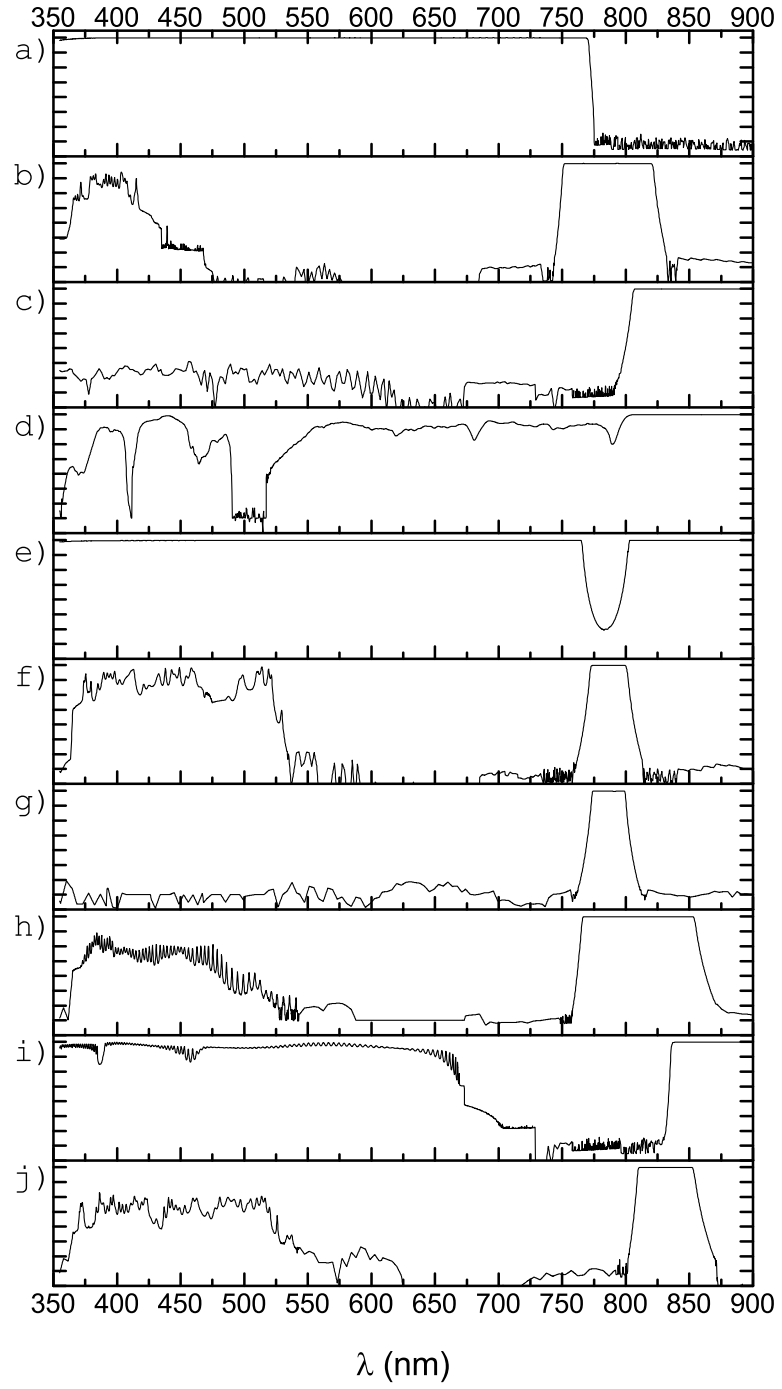


Figure A.3: Interference filter transmission spectra corresponding to Table A.1. Y-axis in in OD (highest tick is OD-0, ticks below go as OD-1, OD-2, etc.). Plots here come from Semrock's average transmission data (see www.semrock.com).

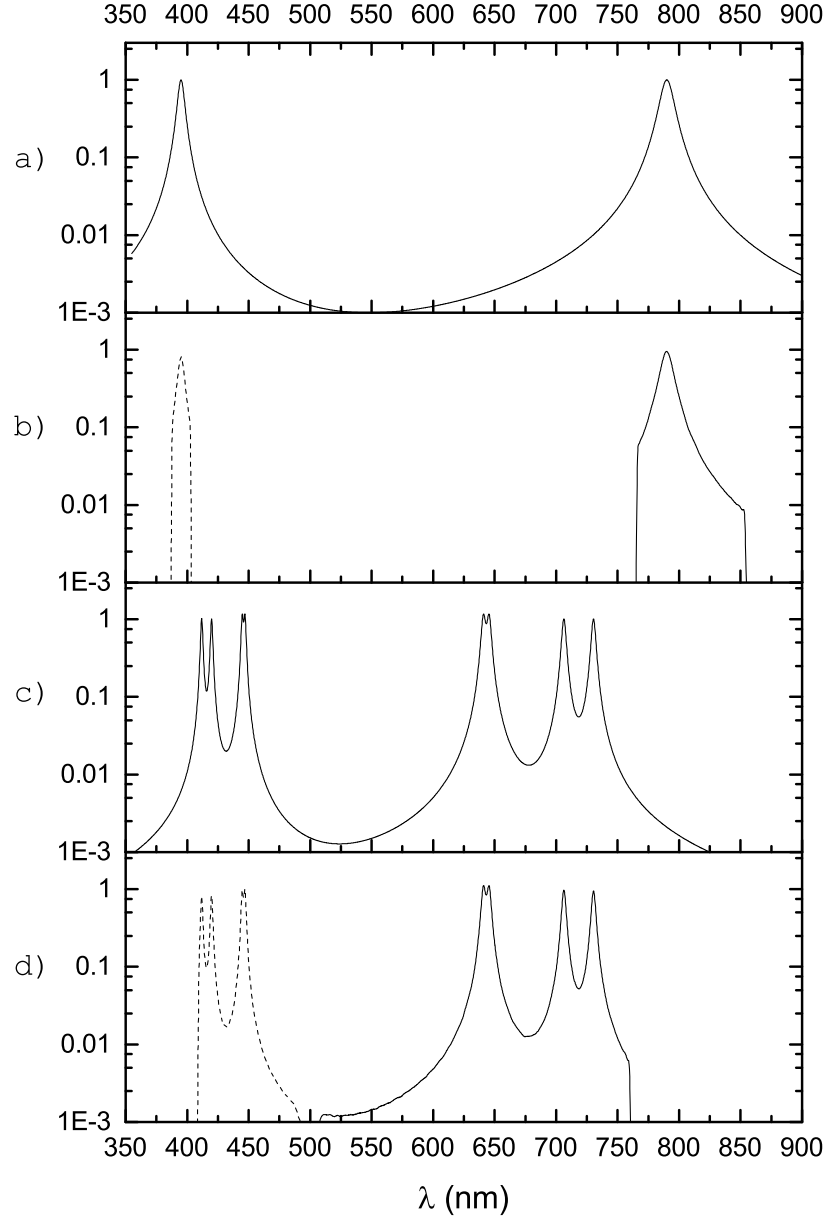


Figure A.4: Example of filtering: a) Fundamental and second harmonic generated (SHG) pumps without filtering. b) Fundamental (solid) cleaned up by application of A.2.d and two A.3.h filters; and SHG (dashed) cleaned up by A.2.d, two A.2.c, and two A.1.b filters. c) Lorentzian modeled Stokes and Anti-Stokes signals without filtering. d) Stokes signal (dashed) cleaned up by A.1.h and four A.1.f filters, anti-Stokes signal (solid) cleaned up by A.1.h and A.2.h filters.

Appendix B

MATLAB ANALYSIS

Through National Instruments LabView software a spectrum is recorded as a row of amplitudes whose position relates to the pixel-bin on the CCD camera. At the head of this row is the numerical position of the linear motion stage, for bookkeeping purposes. The numerical analysis begins by collecting the spectra for specific time delays in a column. The result of this is for a single data collection a $1 + 1024 \times N$ matrix. These are loaded in to the software Matlab. Then to average out background instabilities, cosmic rays, etc. collection sets are compiled together.

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
#####
% Edited by Seth Meiselman for 2015-02-21 data
% analysis for propanol @ 3000cm-1
% 260 time steps of 0.0025 mm on the stage, 0.005 mm delay
% 2 second exposures
% for stokes acquisition temporal arm 6.84mW
% both arms 14.77mW
% for laser acquisition temporal arm 5.08mW
% both arms 11.05mW
% --- measured into sample cell
% last updated 2015-04-22
#####
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% load stokes data files --- from stokes folder
load bkg1.dat;load bkg2.dat;load bkg3.dat;load bkg4.dat;load bkg5.dat;
load bkg6.dat;load bkg7.dat;load bkg8.dat;load bkg9.dat;load bkg10.dat;
load raw1.dat;load raw2.dat;load raw3.dat;load raw4.dat;load raw5.dat;
load raw6.dat;load raw7.dat;load raw8.dat;load raw9.dat;load raw10.dat;

% create signal tensors
sz = size(raw1); ytimepos = zeros(sz(1),2);
laser = zeros([sz,10]); stokes = zeros([sz,10]);
bkg1 = zeros([sz,10]); bkg5 = zeros([sz,10]);
raw1 = zeros([sz,10]); raws = zeros([sz,10]);

% combine stokes files into stokes signal tensors
bkg5(:,1)=bkg1(:,:); bkg5(:,2)=bkg2(:,:); bkg5(:,3)=bkg3(:,:);
bkg5(:,4)=bkg4(:,:); bkg5(:,5)=bkg5(:,:); bkg5(:,6)=bkg6(:,:);
bkg5(:,7)=bkg7(:,:); bkg5(:,8)=bkg8(:,:); bkg5(:,9)=bkg9(:,:);

```

```

bkg3(:, :, 10)=bkg10(:, :);
raws(:, :, 1)=raw1(:, :);   raws(:, :, 2)=raw2(:, :);   raws(:, :, 3)=raw3(:, :);
raws(:, :, 4)=raw4(:, :);   raws(:, :, 5)=raw5(:, :);   raws(:, :, 6)=raw6(:, :);
raws(:, :, 7)=raw7(:, :);   raws(:, :, 8)=raw8(:, :);   raws(:, :, 9)=raw9(:, :);
raws(:, :, 10)=raw10(:, :);

% delete raw data files from memory space
clear bkg1 bkg2 bkg3 bkg4 bkg5 bkg6 bkg7 bkg8 bkg9 bkg10;
clear raw1 raw2 raw3 raw4 raw5 raw6 raw7 raw8 raw9 raw10;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
#####      #####      #####      #####      #####      #####      #####
% load laser data files --- from laser folder
load bkg1.dat;load bkg2.dat;load bkg3.dat;load bkg4.dat;load bkg5.dat;
load bkg6.dat;load bkg7.dat;load bkg8.dat;load bkg9.dat;load bkg10.dat;
load raw1.dat;load raw2.dat;load raw3.dat;load raw4.dat;load raw5.dat;
load raw6.dat;load raw7.dat;load raw8.dat;load raw9.dat;load raw10.dat;

% combine laser files into laser signal tensors
bkg1(:, :, 1)=bkg1(:, :);   bkg1(:, :, 2)=bkg2(:, :);   bkg1(:, :, 3)=bkg3(:, :);
bkg1(:, :, 4)=bkg4(:, :);   bkg1(:, :, 5)=bkg5(:, :);   bkg1(:, :, 6)=bkg6(:, :);
bkg1(:, :, 7)=bkg7(:, :);   bkg1(:, :, 8)=bkg8(:, :);   bkg1(:, :, 9)=bkg9(:, :);
bkg1(:, :, 10)=bkg10(:, :);
raw1(:, :, 1)=raw1(:, :);   raw1(:, :, 2)=raw2(:, :);   raw1(:, :, 3)=raw3(:, :);
raw1(:, :, 4)=raw4(:, :);   raw1(:, :, 5)=raw5(:, :);   raw1(:, :, 6)=raw6(:, :);
raw1(:, :, 7)=raw7(:, :);   raw1(:, :, 8)=raw8(:, :);   raw1(:, :, 9)=raw9(:, :);
raw1(:, :, 10)=raw10(:, :);

% delete raw data files from memory space
clear bkg1 bkg2 bkg3 bkg4 bkg5 bkg6 bkg7 bkg8 bkg9 bkg10;
clear raw1 raw2 raw3 raw4 raw5 raw6 raw7 raw8 raw9 raw10;

```

Since the spectra recorded do not contain the wavelength position (i.e. pixel-bin) for the corresponding amplitudes, these wavelength positions are recorded in a separate file. Then the array of wavelengths is transformed into more useful measures; e.g., wavenumbers or frequency.

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% import wavelength range of spectra
load lambda_cent430_stokes.asc
xlbmdastokes = lambda_cent430_stokes(:, 1);
load lambda_cent390_laser.asc
xlbmdalaser = lambda_cent390_laser(:, 1);
clear lambda_cent430_stokes;
clear lambda_cent390_laser;
% convert spectra in nm into inverse cm
xinvcm1 = 10000000*(1./xlbmdalaser(:)) - 25641;
xinvcms = 10000000*(1./xlbmdastokes(:)) - 25641; %12820.5; %for blue x2
% convert spectra in nm into frequency THz
xomg1 = 299792458*1000000000*(1./xlbmdalaser(:))*1E-12; % nu in THz
xomgs = 299792458*1000000000*(1./xlbmdastokes(:))*1E-12; % nu in THz
%clear xlbmdalaser;% xlbmdastokes;

```

The final initialization steps are to create or convert the time position of a

spectrum and to remove background signal from the pump and Stokes spectra. Below the array of time is explicitly created.

```
% create position array and time delay array
for i = 1:sz(1)
    ytimepos(i,1) = rawl(i,1,1); % position on stage
% step = 0.0025 mm --> '0.005'; delay = 2*step; c in mm/ps = 0.299782458
    ytimepos(i,2) = -(0.005/0.299792458)*(sz(1)/2+8)+(0.005/0.299792458)*i;
end
% this plus 8

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% create background subtracted tensors of (delay,pixel,set)
% subtract farthest time delay from rest of set
for j = 1:10
    for i = 1:sz(1)
        stokes(i,:,j) = raws(i,:,j) - 0.5*(bkgs(1,:,j)+bkgs(end,:,j));
        laser(i,:,j) = rawl(i,:,j) - 0.5*(bkgl(1,:,j)+bkgl(end,:,j));
        %tempbs(i,:,j) = bkgs(i,:,j) - 0.5*(bkgs(1,:,j)+bkgs(end,:,j));
        %tempbl(i,:,j) = bkgl(i,:,j) - 0.5*(bkgl(1,:,j)+bkgl(end,:,j));
    end
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% estimation of avg number of stokes photons
% (sum-floor)/(2sec*80MHz) sum per exposure
% prs = 1 + (spatial arm pwr /temporal arm pwr)
% avg through all delays of data set
% pwr*scale*totalavg avg through data sets*power of both arms
%stokesperpulseavg1 = (sum(bkgs(:,570:730,:),2)-flbkgs*(730-570))/(2*80E6);
%stokesperpulseavg2 = mean(stokesperpulseavg1(:,,:),1);
%stokesperpulseavg = prs*mean(stokesperpulseavg2);
%clear stokesperpulseavg1 stokesperpulseavg2;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
save('prop3_20150221.mat'); % save basic data file
load('prop3_20150221.mat'); % load basic data file
```

The following parameters are created to allocate memory space. This padding of the spectrum increases the numerical Fourier transformation resolution.

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% interpolate data sets to have even freq spacing for FFT
% pad data set with ones(zeros) on both sides to increase FFT resolution
% take fft of each data set -> then average FFT values.
% no smooth using Matt DeCamp's 2D gaussian function --- standardize this
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
padsz = 1536; % 1024 + 512
padstokes = zeros(sz(1),1024+2*padsz,10);
padlaser = zeros(sz(1),1024+2*padsz,10);
intpstokes = zeros(sz(1),1024,10);
intplaser = zeros(sz(1),1024,10);
```

```
fftstokes = zeros(1024+2*padsize,sz(1),10);
fftlaser  = zeros(1024+2*padsize,sz(1),10);
```

Since the spectrometer used measured amplitude as a function of wavelength, the spacing of the frequency or wavenumber array is not uniform. This will cause problems for the numerical Fourier transform, so, to avoid this issue, we reset the spacing in these forms.

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% recast frequency array into even spacing for interpolation of signal
xomgsfixed = min(xomgs):(max(xomgs)-min(xomgs))/1023:max(xomgs);
xomglfixed = min(xomgl):(max(xomgl)-min(xomgl))/1023:max(xomgl);
xinvcmsfixed = min(xinvcms):(max(xinvcms)-min(xinvcms))/1023:max(xinvcms);
xinvcmfixed = min(xinvcm):(max(xinvcm)-min(xinvcm))/1023:max(xinvcm);
```

The numerical Fourier transformation requires a transformation of the frequency domain to the time domain, seen below.

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% FFT transformed 'time' axis from frequency domain Df=Dt=1
spds = 1/((max(xomgs)-min(xomgs))/1023)*(2*padsize+1024));
spdl = 1/((max(xomgl)-min(xomgl))/1023)*(2*padsize+1024));
ys = 0:spds:spds*(1024+2*padsize-1);
yl = 0:spdl:spdl*(1024+2*padsize-1);
%clear spds spdl;
```

We adjust the amplitude of the signal to arrange itself with the evenly spaced frequency domain, and then take the Fourier transformation of the time-delay matrices. Because of phase instability in our system, the individual spectra cannot be averaged together. However, the time domain information they contain, revealed through the real part of the Fourier transform, has no phase information, and thus can be averaged.

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% interpolate signal onto even spacings, pad data set for resolution
for j = 1:3
    for i = 1:sz(1)
        intpstokes(i,:,j) = interp1(xomgs,stokes(i,2:1025,j),xomgsfixed);
        padstokes(i,:,j) = [ones(1,padsize) intpstokes(i,:,j) ones(1,padsize)];
        intplaser(i,:,j) = interp1(xomgl,laser(i,2:1025,j),xomglfixed);
        padlaser(i,:,j) = [ones(1,padsize) intplaser(i,:,j) ones(1,padsize)];
    end
    % take FFT of data sets
    fftstokes(:,j) = fft(padstokes(:,j));
    fftlaser(:,j) = fft(padlaser(:,j));
end
%clear padsize padlaser padstokes i j;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% take average of FFT maps
```

```

avgfft_laser = mean(abs(fft_laser),3);
avgfft_stokes = mean(abs(fft_stokes),3);
%clear intp_stokes intp_laser fft_stokes fft_laser xomgsfixed xomglfixed;

```

The information we are investigating lies along the main diagonal of these two-dimensional time domain plots, where the time delay $\tau = t$ is the Fourier transformed time coordinate. Since the Fourier transformed time coordinate has a higher resolution than our time delay array, and because we cannot manipulate the two arrays to have overlapping identical positions, we must find the points that lie closest to this main diagonal line.

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%take slice along diagonals
sigstokes = (avgfftstokes(1:1500,:))';%shelofs);
siglaser = (avgfft_laser(1:1500,:))';%shelofs);
dlaser = zeros(1,sz(1));
dstokes = zeros(1,sz(1));
for i=1:sz(1)
    dlaser(i) = siglaser(i,find(abs(yl-abs(ytimepos(i,2)))< 0.0018,1));
    dstokes(i) = sigstokes(i,find(abs(ys-abs(ytimepos(i,2)))< 0.0018,1));
end
dlasercorrected = interp1(ytimepos(:,2)*(438.8/384.8)^2,dlaser,ytimepos(:,2));
dsig = dstokes(:)./dlasercorrected(:);
%clear sigstokes siglaser dstokes dlaser dlasercorrected sz;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% END OF FILE
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

```

Finally, to remove spectrometer bias over the different wavelength regions of the pump and Stokes signals we interpolate the main diagonal of the pump after scaling its time domain coordinate. Then the extracted signal is the Stokes signal scaled to that of the interpolated pump signal.

Appendix C

SIMULATION CODING

To start the simulation process we first characterize some physical and numerical constants for the code. The physical constants relate to the experimental parameters used by the motion controller for the mechanical stage and the center frequency and bandwidth of the pump laser field. The numerical constants for the code are for better understanding of relationships and sizes within the code itself. The constant ‘delaypts’ refers to the number of time delays taken via the mechanical stage between the two arms of the interferometer. It is important to note that ‘delaysize’, the physical time delay increment caused by motion of the mechanical stage here is the same for that made during the experiment. For faster beating oscillations or better resolution of possibly highly complex beating patterns a shorter delay would be necessary as would an increase of the number of total delay points taken, ‘delaypts.’

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
####      TCUPS Simulation updated 2015-11-12      ####
####      By Seth Meiselman                        ####
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
                                                    tic % for timing purposes

      ### Empty memory to prevent previous definition problems ###      ###
close all
clear all

      ### Physical experimental parameters ###      ###
delaysize = 0.03333;      %in ps delay stage step size 0.005 mm = 0.01667 ps
                        %0.01667;      %   which is doubled for increase of path length
                        %0.02;

laserfreq= 380; %775;      %in THz c/lambda 775THz = 386.8nm, 380THz = 788.9nm
pulsewidth= 0.150;      %in ps laser duration length of approx 150 fs

      ### computational constant parameters ###      ###
stepsize= 0.00015;      %in ps of time points for input laser field
kbit = 2^11;      %   integer count used throughout code
byte = 2^13;      %   integer count used throughout code
kbyt = 2^15;      %   integer count used throughout code
delaypts= 500;      %   delay stage steps, this must be even

```

The ‘stepsize’ is the initial resolution used for the creation of the oscillating pump laser field. The number of total time points for the pump field as labeled is $2 \times \text{‘kbyt.’}$

```

    % Discretization in time
    time=-kbyt*stepsize:stepsize:(kbyt*stepsize-stepsize); %in ps
    timesteps=max(size(time));
    % Full time length
    timewindow=2*max(time); % (2^16)*stepsize

```

From the initial time domain, defined by the total length and the length of the resolving step size we can then create a Fourier transformation into the frequency domain. The resolution of this frequency domain is the inverse of the total length of the time domain and then is converted into a common cm^{-1} spacing given by ‘dcm’ whose vector is given by ‘wcmaxis’. The frequency points in ‘wcmaxis’ are limited to a range of around the pump laser frequency for conservation of memory space further in the code.

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
    % Fourier transform requires even number of points
    % Fourier transform from real time to spectrum frequency
    % Fourier frequency resolution and length
    vsignalaxis=0:1/(timewindow):(timesteps-1)/timewindow;
    wcmaxis= 100*vsignalaxis/3; % Freq length in inverse cm
    dcm=wcmaxis(2)-wcmaxis(1); % Freq resolution in inverse cm
    % Limit of fourier frequency axis to span laser spectrum
    wcmaxis=wcmaxis((10*laserfreq-kbit/2):(10*laserfreq+kbit/2-1));
    clear vsignalaxis wcmaxis;

```

Again a Fourier transformation is taken from the cm^{-1} frequency domain toward what we’ll label the FT-time domain. This is to differentiate between it and the “real time-domain,” which corresponds to the delays set between the two arms of the interferometer described in Section 2.1.

```

    % Fourier transform from spectrum frequency to FT time
    % Fourier time resolution and length
    deltawin=dcm*kbit; % Fourier transform window length
    timewin=(0:1/deltawin:1/deltawin*(kbit-1))*(100/3); % Fourier time steps

```

We now create the function in time of the pump laser. In the simulation results seen here we used Gaussian envelope pulses, without chirp effects, centered at zero with a lasing frequency shown above.

```

    % Define field envelope lineshape functions
    sig= @(d) (d/2.3548);
    gaussian= @(x,cntr,d) exp(-(x-cntr).^2/(sig(d)^2)); % not unitary
    %lorentz= @(x,cntr,d) (1/pi)*((d/2)./( (x-cntr).^2+(d/2)^2));
    field= @(x) sin(laserfreq*2*pi.*x);

```

```

        % Laser as a function of time and frequency %
        laserint= gaussian(time,0,pulsewidth).*field(time);
        %fft laserint=abs(fft(laserint)); % single beam on spectrometer

```

Creating stage delays in time via ‘delay’ we construct the time delayed laser field, and then combine them with the undelayed pump field in ‘laserfield.’ The observed spectrum of the combined beams on the detector is shown by ‘fft laser,’ which is a limited window of the whole transformation space, again to save memory and increase speed.

```

        % Make delayed laser fields for all stepsize delays %
        ffttimelaser= zeros(delaypts,timesteps); % memory allocation
        delaytime= zeros(1,delaypts); % memory allocation for following loop
        for t=1:delaypts
            delay=(t-delaypts/2)*delaysize; % for pos and neg delays
            % Delayed laser as a function of time %
            delaylaserint= gaussian(time,delay,pulsewidth).*field(time-delay);
            % Recombination of interferometrically delayed beams %
            laserfield = laserint + delaylaserint;
            delaytime(t)=delay; % axis range definition
            % Intensity in frequency space of total laser field %
            % This would be what is observed on the spectrometer %
            ffttimelaser(t,:)=abs(fft(laserfield)).^2;
        end;

        toc % for timing purposes

        % Limiting window of spectrometer data to save memory %
        fftlaser=ffttimelaser(:,(10*laserfreq-kbit/2):(10*laserfreq+kbit/2-1));

        % Clean up memory space by removing large objects that are unneeded %
        clear ffttimesignallaser delay delaylaserint laserfield laserint;

```

We create the Raman tensor in two steps. First is the description of the modes themselves: center frequency, relative amplitude, and approximate widths. These could be refined or even substituted with reported values in the literature. However, for the main purpose of this code, to show the results of the interference and thus beating between modes, approximate values are sufficient.

```

        % mode# = [ cntr#/deltacm, amp#, width#/deltacm]; %
        mode0 = [0,0,0];
        % propanol modes %
        mode1 = [2880.1/dcm, 0.21, 10/dcm]; % 27 in wavenumbers
        % mode2 = [2924.7/dcm, 0.99, 35/dcm];
        mode3 = [2928.0/dcm, 0.48, 30/dcm]; % 49
        % mode3 = [2937.0/dcm, 0.20, 34/dcm];
        mode4 = [2978.0/dcm, 0.31, 7/dcm]; % 23
        % methanol modes %
        mode5 = [1034.0/dcm, 0.39, 25/dcm]; % in wavenumbers
        mode6 = [2835.0/dcm, 0.19, 20/dcm];
        mode7 = [2945.0/dcm, 0.10, 25/dcm];

```

The second part is to construct the Raman tensor itself. This is done in the code below for up to four modes. The tensor used in the results here is created with Lorentzian modes for a specified frequency window. For calculation simplicity and speed, the discretized Raman tensor is truncated with a floor value.

```
function output=ramantensor(inputsize,model,model2,model3,model4);
cntr1 = model(1); amp1 = model(2); width1 = model(3);
cntr2 = model2(1); amp2 = model2(2); width2 = model2(3);
cntr3 = model3(1); amp3 = model3(2); width3 = model3(3);
cntr4 = model4(1); amp4 = model4(2); width4 = model4(3);
%sig= @(d) (d/2.3548);
%gaussian= @(x,cntr,d) exp(-(x-cntr).^2/2/sig(d)^2); % not unitary
lorentz= @(x,cntr,d) (1/pi)*((d/2)./( (x-cntr).^2+(d/2)^2));
x=1:inputsize;
output=sparse(inputsize,inputsize);
for i=1:(inputsize)
    center1 = i+cntr1; center2 = i+cntr2;
    center3 = i+cntr3; center4 = i+cntr4;
    trans1 = amp1*lorentz(x,center1,width1);
    trans2 = amp2*lorentz(x,center2,width2);
    trans3 = amp3*lorentz(x,center3,width3);
    trans4 = amp4*lorentz(x,center4,width4);
    % trans1 = amp1*gaussian(x,center1,width1);
    % trans2 = amp2*gaussian(x,center2,width2);
    % trans3 = amp3*gaussian(x,center3,width3);
    % trans4 = amp4*gaussian(x,center4,width4);
    transition = trans1 +trans2 +trans3 +trans4;
    zerotrans =find(transition>.001);
    output(zerotrans,i) = transition(zerotrans);
end
```

Then by taking the vector product of the frequency-resolved laser spectrum and Raman tensor for a set of modes we create the expected signal output for the range of time delays between the two pump laser beams. Further removing a background signal from the set of delays allows better comparison of the simulation results and the experimental data.

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%% Propanol Raman tensor and signal creation %%%
%%% Create Raman tensor with given modes %%%
raman=RamanTensor(kbit,model,model3,model4);
ramanspec = zeros(delaypts,kbit); % memory allocation for following loop
for i=1:delaypts
    ramanspec(i,:)=abs(fft(laser(i,:)*raman).^2); % spectrum output vs delay
end
fftsig=abs(fft(ramanspec')); % FFT of spectrum vs delay
toc % for timing purposes
%%% Background subtraction from spectrum %%%
%bkgsubtract=zeros(delaypts,kbit); % memory allocation for following loop
fftbkgsig=zeros(kbit,delaypts); % memory allocation for following loop
for i=1:delaypts
    %bkgsubtract(i,:)=(ramanspec(i,:)-ramanspec(1,:))./max(ramanspec(1,:));
```

```

        fftbkgsig(:,i)=(fftsig(:,i)-fftsig(:,128))./(max(fftsig(:,128)));
    end
    % fftbkgsig=abs(fft(bkgsbtract')); % background subtracted FFT of spectrum

```

Now begins the basic plotting sequence for both the 2D Fourier-transformed spectra and their main diagonals corresponding to $t = \tau$, see 2.2.

```

figure(100);
subplot(2,1,1);
    surf(delaytime,timewin,fftsig); view(2); shading flat;
    line([0 2],[0 2],[1e12 1e12],'color','w','linestyle',':');
    line([0 -2],[0 2],[1e12 1e12],'color','w','linestyle',':');
    axis([-2 2 0 2]); caxis([0 6.5E11]);
    title('propanol 3 peaks simulated FFT signal');
    xlabel('Time[ps]'); ylabel('Time[ps]');
subplot(2,1,2);
    surf(delaytime,timewin,fftbkgsig); view(2); shading flat;
    line([0 2],[0 2],[1 1],'color','w','linestyle',':');
    line([0 -2],[0 2],[1 1],'color','w','linestyle',':');
    axis([-2 2 0 2]); caxis([0 0.25]);
    title('propanol 3 peaks simulated FFT signal (bkg subtracted)');
    xlabel('Time[ps]'); ylabel('Time[ps]');

```

The last part of note is the determination of the main diagonal for comparison. To do this we pick out the points that lie closest to the line $t = \tau$.

```

dtimewin = (max(timewin)/length(timewin));
ddelaytime = (max(delaytime)*2/length(delaytime));
stepconv=dtimewin/ddelaytime;
clear dtimewin ddelaytime;

diag1=zeros(1,delaypts);
for i=1:delaypts
    diag1(i)=fftbkgsig(abs(floor(delaypts/stepconv/2-i/stepconv))+1,i);
end
diag1=diag1./max(diag1);

load('propdata.mat');
figure(101);
semilogy(delaytime,diag1); axis([-2.5 2.5 1E-2 2]);
title('propanol 3 peaks');
hold on;
semilogy(propdata(:,1),propdata(:,2),'r');
hold off;

toc % for timing purposes
#####
#####      END OF FILE      #####
#####

```

The creation of the Raman tensor and signal output can then be performed sequentially for all systems of interest. The explicit parameters for the numerical simulation outlined here were used to generate quick yet qualitatively correct results, using a reasonable amount of memory space. As such, there are remnants of the numerics. The

most distinct is at the bottom of the two dimensional plots, per the settings used this feature shows up in all tested outputs. This is due to the spacing of the original time domain for the electric field and the corresponding spacing of the Fourier transformation coordinates in the frequency domain. A second numerical result shows up in the form of other orders of the expected signal through the numerical Fourier transformation. This is due to the purity of the computational waveforms generated at the start of the simulation. It is expected that a simulation expressing realistic signal-to-noise would suppress these features.