ULTRAFAST MEMORY LOSS AND ENERGY REDISTRIBUTION IN THE HYDROGEN BOND NETWORK OF LIQUID H₂O

by

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

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Using two-dimensional infrared spectroscopy, this work has dissected the intermolecular dynamics in the fully resonant hydrogen-bonded network of liquid H₂O. This work involved the development of new infrared laser sources with sufficient (μJ) pulse energies, as well as an experimental apparatus suitable for performing phase sensitive infrared (IR) spectroscopy. In particular, the development of a diffractive optics based experimental setup for use in the IR, as well as nanofluidics for handling the strong absorption of pure H₂O, were found to be necessary for extracting the relevant water dynamics, and are described in detail. Resonant energy transfer on a 100 fs time scale is observed in H₂O, as well as extremely fast spectral diffusion that results in a spectral sweep in the OH frequencies on a 50 fs time scale. There is an equally fast dephasing process observed in the system, leading to a near complete loss of inhomogeneity within 50 fs. The net effect is a very efficient redistribution of energy in liquid water. These results are in dramatic contrast to studies of isotopic water and clearly illustrate the importance of studying pure liquid H₂O directly. These findings lead to new appreciation of the significance of fully resonant conditions for energy exchange and coupling among different degrees of freedom that can only be probed for pure H₂O.
Acknowledgements

Graduate work is not a straightforward route to producing a thesis, rather, it is a significant stage in a person’s life. As you might guess, this will not be your standard book dedication. If I wanted to write a book, I could have done it in a lot less time than it took to bring this thesis to fruition. A book is something you write, but a thesis is something you live. Choosing to write one essentially defines everything you are for a period of several years – more so than just the hours you work or the colleagues whose company you keep – from the money you are capable of bringing in (not much), to the lifestyle you can afford to live (see previous), to the friends you feel comfortable in keeping (i.e. absent-minded, slack-off academics; other students, people without real jobs such as yourself). You can’t sum up a life in merely 200 words and a shout-out to your parents. I have no intention of trying to be completely thorough (I wrote one thesis already!), but I will require a lot more than 200 words.

My grad school career can be roughly divided into thirds. The first third was a time for rolling in money (er, relatively speaking), waterfall-sized deluges of exciting new laser projects, and trying to learn a million new things at once. The second third was a time for extracurricular activities (both political and social), feeling like a carefree student, meeting some very nice young women, and frustratingly slow progress in the lab. The final third was crunch time – regaining my stride in my research, fantastic new collaborations, and finally, writing this thesis. It’s probably not an accident that each of three phases featured a mutually exclusive cast of characters/friends, co-workers, and even research projects. On the other hand, it’s probably a complete coincidence that each phase happened to take up approximately the same amount of time.

However, a number of very special people figured prominently into all three phases of this thing I call graduate school life, and for that I want to thank them separate from all the others. First, naturally, I want to thank my Masters and Ph.D. supervisor, Dwayne Miller. Dwayne’s unending enthusiasm for his work, and his singular ability to pass that
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By my count, there have been forty other full-time Miller Group members during my time here. Some of them contributed significantly to my development as a scientist and I want to highlight them here. Dividing this time into phases:

Phase One

Visiting Professor Zhen Guo might taught me a critical and very underrated lesson –
how to take things apart and put them back together again without the slightest hint of fear or apprehension. I still have his Chinese-English dictionary, which he asked me to safeguard for him until his next visit to the group. If I don’t hear from him in the next couple of months, that dictionary might have to leave with me. Evgeuni Slobodchikov is a meticulous worker and a patient teacher. Put him in front of an optical table and you can watch a real wizard at work. The Cr:Forsterite work had its genesis thanks to him. I worked closely with Jiaren Liu and Yan Liao on several laser development projects and benefited greatly from their extensive laser-related experience. David Miller and John Montgomery, then working at Lumonics Inc., took me under their wing during my internship there in 1998. I’m grateful to them for taking the time to teach a novice a bunch of useful and fascinating laser research (and industry) tricks. Under their supervision, my work on nanosecond pulse shaping was probably my most successful project during Phase One.

Phase Two

I want to thank optimism.

Phase Three

I am indebted to Professor Thomas Elsässer and Dr. Erik Nibbering for welcoming me into their lab at the MBI in Berlin. Collaborating with their research group was invaluable in the completion of this thesis. Dr. Michael Cowan was my partner in crime during most of Phase Three and he is by far the sharpest scientist that I’ve ever worked with. Nils Huse’s lab smarts are outdone only by his work ethic. I was very fortunate to work with Michael and Nils, who are not only a couple of great physicists but are also a blast to hang around with. Both qualities are crucial when one needs to lurk in the lab taking data for days at a time.

To all people and things that provided a welcome distraction from physics over the past several years – please accept my thanks as well as your share of the blame.
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Chapter 1

Introduction

Water has a number of unique features that distinguish it from other liquids and provide it with its life giving properties. Because of water's relevance in a great number of scientific fields, particularly in biophysics and biochemistry, understanding its properties is a matter of considerable importance. For these reasons, water has been the focus of intense and thorough experimental characterization [1, 2].

Water can be so curious and complex that in certain cases even seemingly simple problems have non-trivial solutions. For instance, it was less than a decade ago that a clear understanding of the physics of ice skating began to emerge. Pressure melting used to be frequently cited as the mechanism that caused the ice surface to liquefy, thereby making skating possible by reducing the friction between ice and the skate blade. This explanation stubbornly persisted even though one discovers, via a very simple calculation, that the pressure caused by a skate blade is two or three orders of magnitude too small to liquefy ice. It was then suggested that frictional heating is the dominant process driving the liquefaction [3]. The current understanding, which comes from low energy electron diffraction studies that probe the surface properties of ice, is that the top surface layer of ice remains liquid-like well below 0°C [4, 5, 6]. This would not only explain the physics of ice skating, but would also account for the reason why ice is so slippery.
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There is considerable motivation behind the effort expended in this thesis work. Water has been the subject of considerable theoretical interest, with a great deal of research directed toward modelling water on the molecular level. By postulating or calculating its electronic structure and the intermolecular potentials between molecules, these models have attempted to calculate macroscopic properties of water such as its dielectric constant and its density \cite{7, 8}. These are complex problems because water has many anomalous properties in comparison to other liquids. In many cases, molecular-level explanations of these anomalies are still lacking. The density problem is probably the most well-known of these. During the transition from ice to liquid water, the density increases and reaches a maximum at 4°C. In contrast, the density of most substances decreases during melting and continues to decrease during heating and thermal expansion. Any veritable theoretical model for water must be capable of offering some explanation for this unusual behaviour.

In the current picture, the special properties of liquid water are directly connected to the hydrogen bond network. A hydrogen bond forms due to an attractive electrostatic force that occurs between a hydrogen atom and a heavy, more electronegative atom such as oxygen, nitrogen, or fluorine. Liquid water molecules have a high affinity for each other, with each molecule capable of forming up to four hydrogen bonds with its neighbours. Furthermore, this complicated hydrogen bond network can also fluctuate in time, modulating orientational properties of the molecules such as the dielectric relaxation time.

In general, these molecular motions in water occur on picosecond or subpicosecond time scales. Thus, understanding the structure and dynamics of the hydrogen bonded network necessitates measuring dynamical processes on the time scale of the hydrogen bond fluctuations, and preferably faster. At present, only femtosecond infrared lasers can be tuned to the wavelengths of vibrational transitions while producing pulses that are short enough to meet these time resolution requirements. Therefore, in order to obtain
information on the hydrogen bond network in water or in virtually any other biological
system of interest, development of appropriate infrared laser sources is crucial.

In particular, from a spectroscopy standpoint, many features in the infrared and
Raman spectra of water are in need of a more complete explanation. The gas phase
spectrum of water is made up of many thousands of narrow spectral lines [9]. In compar­
ison, the liquid spectrum consists of broad spectral peaks. The most prominent feature
in its infrared absorption spectrum occurs in the OH-stretch region, which contains a
single extremely broad peak centred near 3400 cm$^{-1}$ with a width of about 250 cm$^{-1}$.
In comparison, virtually all vibrational modes in other condensed phase systems have
a linewidth more than an order of magnitude smaller. The few exceptions also include
some degree of hydrogen bonding. The linewidth in all cases involving hydrogen bonding
is anomalously broad compared to any other substance.

The physical cause for the anomalously broad OH-spectrum of water is one of the
oldest unsolved problems in spectroscopy and has defied full explanation for decades.
Recognition of the problem dates back to at least the 1930’s, to the liquid water Raman
studies of Cross et al. [10] as well as the first X-ray diffraction experiments on water
performed by Morgan and Warren [11]. It has long been understood that the OH stretch
vibration is coupled to the hydrogen bond network in water [1]. In fact, some of the
earliest research on the very concept of hydrogen bonding were attempts to explain
various unusual properties of water. Latimer and Rodebush’s examination of water’s
high dielectric constant, in work dating back to the 1920’s, stands out in this respect [12].
Directly probing the OH-stretch region of water should provide a direct window on the
dynamics of its H-bond network and intermolecular couplings.

The key question regarding the spectroscopy of the OH-stretch region in water is
centred upon the broadening mechanisms that lead to such an anomalously broad spectral
feature. This can occur due to homogeneous broadening, inhomogeneous broadening, or
some combination of the two. In other words, to what degree is the broadening due
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to static, or inhomogeneous mechanisms; and to what degree is it due to dynamic, or homogeneous mechanisms? The former process is the result of local substructures of water molecules that do not change with time, whereas the latter process is the result of couplings between molecules that result in time-dependent changes in local substructures as well as reconfigurations in the hydrogen bond network on time scales fast enough to average out the structural variations. This information can in turn be related to intermolecular forces and anharmonic couplings, as well as to molecular and hydrogen bond dynamics.

These questions can be addressed using multidimensional infrared spectroscopy. 2D-IR is an optical analogue of 2D-NMR spectroscopy and can directly measure the intermolecular coupling between molecules, much like NMR does in revealing couplings between nuclear spins. The shapes and spectral positions of the peaks in 2D-IR spectra contain information about the intra and intermolecular couplings in the sample as well as the degree of homogeneous and inhomogeneous broadening that is present in the system of interest. This information is critical in order to experimentally determine the many-body potential of H_2O and, in turn, to understand water's special properties.

The remainder of this thesis will detail the considerable experimental and technical challenges that are prerequisites to performing ultrafast infrared echo experiments on water, followed by, naturally, a presentation and discussion of the key results. The following chapters are organized as follows:

Chapter 2 discusses the generation of femtosecond mid-IR pulses. Chromium-doped forsterite lasers are presented as alternative source lasers to Titanium-doped sapphire systems for generating short mid-IR pulses. Phase-matching and gain calculations indicate that extremely broad amplification bandwidths are possible in parametric amplifiers that are pumped at the 1.25 μm wavelength of Cr:forsterite lasers. An OPA was constructed for this purpose using an in-house design and its performance is reported.

Chapter 3 provides some background to echo and multidimensional infrared spectro-
scopies. Experimental details such as pulse sequences and detection methods are also discussed. In particular, the technique of heterodyne detection using spectral interferometry is highlighted.

Chapter 4 addresses the experimental design and the use of diffractive optics (DO) in generating phase-locked pulses necessary for doing echo spectroscopy. The use of the echo setup for pulse characterization is also detailed. Finally, a short section describing 2D-IR measurements on acetic acid dimers demonstrates the effectiveness of the DO setup for performing phase-sensitive nonlinear spectroscopies.

Chapter 5 provides a more thorough introduction to the long-standing problem of determining the structure of liquid water on femtosecond time scales. Previous attempts to elucidate some understanding of the ultrafast structure and dynamics of water molecules are reviewed.

Chapter 6 begins by detailing our first 2D-IR experiments on water. Particular emphasis is placed on the development of a new sample cell so that the 2D spectra are free of signal contamination from sample cell windows. This leads to the design and construction of new cells with very thin Silicon Nitride windows. This is followed by details of the 2D-IR and transient grating experiments performed with the Silicon Nitride cells, followed by a detailed discussion of the experimental data. Finally, there is a section dedicated to the conclusions and a vision for future work.
Chapter 2

Generating Mid-Infrared Pulses for IR-Spectroscopy

2.1 Mid-IR pulse generation using Ti:Sapphire lasers

Many fields of spectroscopy require laser pulses at mid-infrared wavelengths. Because the fundamental lasing wavelength for most mode locked lasers falls in the visible or near infrared, generating pulses in the mid-IR often requires nonlinear wavelength conversion. Free Electron Lasers are an exception in that their fundamental lasing wavelength can be tuned to the mid-IR, but they are tremendously complex and expensive systems [13]. In practical terms, lasers suitable for laboratory use need to be tabletop-based setups. To reach the mid-IR via nonlinear downconversion, intense, amplified ultrashort pulses are required. Before femtosecond regenerative amplifiers (RGAs) became readily available, this wavelength conversion process was commonly accomplished using Optical Parametric Oscillators pumped by mode-locked picosecond Nd-based lasers. But compared to femtosecond pulses, the lower intensity of the picosecond pump pulses means that the conversion to the mid-IR is much less efficient. Also, the longer picosecond pulses result in poorer time resolution for use in ultrafast spectroscopy experiments [13, 14].
CHAPTER 2. GENERATING MID-INFRARED PULSES FOR IR-SPECTROSCOPY

With the wide availability of Ti:Sapphire (Ti:S) RGAs, wavelength conversion into the infrared became far more straightforward. However, Ti:S lasers operate at 800 nm, which is far removed from the $\sim 2-10 \mu m$ range that is typically used for infrared spectroscopies on molecules of chemical and biological interest. Conversion to the mid-IR has been demonstrated using only one OPA conversion step, but such methods are extremely inefficient [15] and/or do not provide a wide tuning range of mid-IR wavelengths [16]. Accessing a broad wavelength range as well as generating the microjoule energies that are needed for nonlinear spectroscopy usually involves more than one Optical Parametric Amplifier (OPA).

Schematically, a very common cascaded OPA scheme of this sort is depicted in Figure 2.1. First, a small fraction of the RGA output (usually 1-2 $\mu J$) is split from the main beam and focused into a nonlinear medium to produce a white light continuum. The first OPA stage is seeded by this continuum and pumped by a portion of the 800 nm RGA output. The continuum is typically generated in a thin ($\sim 1-3 \text{ mm}$) window of a standard optical material such as sapphire, CaF$_2$, or BaF$_2$. The combination of short RGA pulses ($\leq 100$ fs pulse widths are common) and excellent mode quality easily provides enough intensity to generate a continuum covering the visible and near-IR even with such low energy pulses. Near-IR signal and idler beams are generated via a parametric interaction with the pump and seed beams inside a nonlinear crystal. These beams are generated in the 1.2 - 2.5 $\mu m$ range. Often, the signal and idler beams are amplified further using one or more single-pass stages, with each stage pumped by separate fractions of the 800 nm RGA output. The efficiency of the RGA to near-IR (signal plus idler energy) conversion process is usually around 10%.

The signal and idler outputs from the first OPA are then difference-frequency mixed in another nonlinear crystal. The crystal choices for this difference-frequency generation (DFG) stage are more limited than for the first OPA stage. AgGaS$_2$ [17] or GaSe [18] are particularly common in IR OPAs due to their broad transparency range and reasonably
Chapter 2. Generating Mid-Infrared Pulses for IR-Spectroscopy

Figure 2.1: A schematic box diagram of mid-IR pulse generation using Ti:S RGAs. The first OPA is seeded by a white light continuum, yielding mid-IR signal and idler pulses. The signal and idler are then mixed in a difference frequency generation crystal in order to produce mid-IR light.

high nonlinearity. The typical overall efficiency (RGA to mid-IR output energies) is in the $0.5 - 1\%$ range. This is rather inefficient, but a Ti:S RGA with $1$ mJ output pulses will still generate $5 - 10$ $\mu$J mid-IR pulses, which is sufficient energy for performing most nonlinear experiments. Of course, there is considerable variation in the exact details of these Ti:S-based mid-IR pulse generation methods, but nearly all of them rely on some sort of cascaded OPA scheme in the manner described [17, 19, 20, 21]. Each nonlinear wavelength conversion step is about $10\%$ efficient. This essentially clamps the Ti:S-to-mid-IR efficiency for all methods that require cascaded OPAs at $\sim 0.5 - 1\%$. The book by Zhang et al. [22] offers a thorough review of the various Ti:S-based wavelength conversion schemes and nonlinear crystals that are commonly used.

The efficiency in a single stage is only $\sim 10\%$ because very large amplification in a single stage is normally not possible due to two photon absorption of the 800 nm pump beam in the nonlinear crystal. Weak parametric downconversion of the pump light is possible with high enough intensity, and this process will compete with amplification at
the desired continuum wavelengths. This limits the degree to which the pump beam can be focused and in turn, limits the parametric gain. This favours methods where the amplification takes place in one (or two) preamplification stages followed by a larger power amplification stage. The tightest pump beam focus will then occur in the preamplification stages in order to get the highest gain to build up the seed pulse intensity to levels above that of the parametric noise.

As stated previously, there are many variations on this method. For instance, Gale et al. used a two stage amplifier based on the nonlinear crystal BBO [19]. With this scheme, about half of the 800 nm RGA output is doubled and subsequently used to pump a white light seeded OPA pumped at 400 nm. The idler beam from this OPA is then mixed with the second half of the original 800 nm RGA output. Unlike the cascaded OPA method described above, the wavelength of one of the beams never changes - only the idler wavelength used to mix with the 800 nm pump beam is tunable. This limits the tunability of the final mid-IR pulse. Nonetheless, this scheme is quite effective at reaching the 2.6 – 3.6 μm range with relatively high (≥ 10 μJ) pulse energies. The overall (RGA-to-mid-IR) efficiency is still in the 2% range and the total gain is still limited by the maximum possible pump intensity that must be clamped due to the competing effects of two-photon absorption and parametric downconversion.

2.2 Chromium-doped forsterite lasers as an alternative to Ti:S

Many of the limitations that arise when using Ti:S lasers and amplifiers for mid-IR pulse generation stem from the relatively short lasing wavelength of Ti:S, which requires two parametric downconversion stages in order to reach the mid-IR. Lasers with longer wavelengths have a natural advantage over Ti:S in that it can be possible to convert from the oscillator/RGA wavelength directly into the mid-IR in one parametric step instead.
of two. This led us to investigate other near-IR laser sources. Instead of using amplified Ti:Sapphire at 800 nm, we constructed an oscillator/amplifier system based on the crystal chromium:forsterite.

![Absorption and fluorescence spectra for chromium-doped forsterite](image)

Figure 2.2: Absorption and fluorescence spectra for chromium-doped forsterite. The figure is reprinted with permission from reference [23], copyright 1988, American Institute of Physics.

Lasing in Cr:forsterite was first reported by Petrićević et al. in 1988 [23, 24]. The main advantage of this crystal is its broad tuning range in the near-infrared, which is not easily accessible via other lasing materials. Like Ti:Sapphire, the four-level vibronic structure of Cr:forsterite is responsible for its wide tunability [25]. Absorption and fluorescence spectra for Cr:F appear in Figure 2.2. Note that the fluorescence spectrum covers the 1.1 – 1.3 µm region in the near IR, in the same range as the signal wavelength in most Ti:S-pumped OPAs. In this sense, it is possible to convert the output of a Cr:F laser directly into the mid-IR via one parametric step, as depicted in Figure 2.3.

In subsequent years, Kerr Lens Modelocking (KLM) [26, 27] and passive mode locking using semiconductor saturable absorber mirrors (SESAMs) [28] have been demonstrated. With the KLM method, sub 30-fs pulses have been generated, corresponding to about 70 nm of bandwidth near a central wavelength of 1250 nm for a Gaussian pulse. With
Figure 2.3: A schematic box diagram of mid-IR pulse generation using Cr:FGRGAs. A white light continuum is produced by focusing a portion of the RGA output into a nonlinear medium. The continuum then acts as the seed pulse in an OPA to produce the mid-IR output.

saturable absorbers, the pulse width is usually longer in comparison to KLM for many types of mode locked lasers [29], although sub-100 fs pulses are easily achievable. This limitation is usually due to the reflectivity bandwidth of the SESAM. For instance, 20 fs pulses in Cr:F have been produced using SESAM's with extremely high reflectivity from 1.1 - 1.5 μm [30].

Even more recently, the development of double-chirped mirrors [31] has enabled the generation of even shorter pulses, mimicking similar developments in Ti:Sapphire oscillators. The minimum pulse width achieved to date is 14 fs [32].

The home-built oscillator in our lab is similar to that reported by Guerreiro et al. [28], but was adjusted to operate in the soliton mode-locking regime [31]. The essential difference between the KLM and soliton mode locking regimes is the larger spacing between the intracavity prisms, which produces the larger group velocity dispersion (GVD) necessary for soliton mode locking. The oscillator is passively mode locked using a slow saturable absorber mirror, the physics of which are detailed in the paper by Kärtner and
2.2.1 Cr:F regenerative amplifier

The RGA cavity is shown in Figure 2.4. The z-cavity configuration is similar to those used in Ti:S RGAs, with a total cavity length of 1.5 m. The RGA is pumped with 5.0–7.0 W from a home-built Q-switched laser based on Nd:YLF with a repetition rate of 1 kHz. The laser head employs a Quantronix Nd:YLF flow chamber. A 15 cm lens focuses the pump beam down to a spot size of 80-100 μm. The amplification crystal is Brewster-cut, with dimensions 5x5x18 mm, and is clamped on all four axial sides in a copper holder in order to provide effective heat-sinking. The crystal is water cooled at approximately 15 °C and its temperature is stabilized to within 0.1 °C with a TEC cooler.
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The main difference between this amplifier and more common ones such as Ti:S is the pulse timing/switching mechanisms. It is common to have a quarter wave ($\lambda/4$) plate in the RGA cavity so that during the time when the pulse is circulating in the cavity, the pulse experiences two quarter-wave rotations from each of the Pockels Cell and the $\lambda/4$ plate, once before and once after bouncing off the end mirror. The total polarization rotation is 360 degrees per cavity round trip, and the pulse remains in the cavity as long as the Pockels cell remains “on”. However, the single pass gain in Cr:F is much lower than in Ti:S [33]. The single pass small signal gain at our pump intensity is $\sim 1.5$, compared to $\sim 4$ for comparable Ti:S systems. For this reason, it is advantageous to have fewer intracavity elements. Quarter wave plates can be quite lossy (5% per round trip), plus there will also be non-negligible loss per round trip due to polarization rotation dispersion. That is, the quarter-wave rotation is only exact for one wavelength, so for a broadband pulse the rotation in both the $\lambda/4$ plate and the Pockels cell will be inexact over the entire spectral bandwidth, leading to increased losses when the amplified beam hits the polarizer. In order to maximize the single pass gain, operating without a quarter-wave plate is preferable. Since the double-pass combination of the $\lambda/4$ plate plus the Pockels cell typically accounts for the full rotation that is necessary to trap the pulse during each round trip, it is clear that without a $\lambda/4$ plate the operation of the Pockels cell must also be changed. The normal Pockels cell switching procedure is detailed in, for instance, the book by Koechner [14].

With an Cr:F RGA, the polarity of the Pockels cell is the opposite of the situation described above. The polarization is rotated by the Pockels cell in order to trap it in the cavity. At this point, the high voltage is switched off and the polarization is not rotated at all for each round trip. This avoids the losses associated with polarization rotation error for broadband pulses during each round trip since there will not be any frequency dispersion of the polarization rotation angle each time the pulse passes through the $\lambda/4$ plate or the Pockels cell. No wasted energy will be expelled by the polarizer.
Thus, the Pockels cell starts in its “high” state (at the $\lambda/4$) voltage. Once the seed pulse enters the cavity, the voltage drops to zero and the seed pulse remains trapped. To switch out the pulse, the voltage is increased from zero back to the $\lambda/4$ voltage, and after double passing the Pockels cell the pulse polarization is rotated by $\lambda/2$ and is ejected via reflection from the polarizer. The input and output beams travel the same path but are polarized orthogonal to each other. The combination of a Faraday rotator with a polarizing beam cube allows for the beams to be separated at the latter optic. This combination also provides nearly 1000:1 contrast, thereby preventing the RGA output from leaking back to the oscillator.

The timing unit for the Pockels cell was custom designed and built for this system in cooperation with Quantum Technologies. The Pockels cell was a 15 mm long BBO crystal. BBO has an extremely high damage threshold and experiences negligible piezoelectric ringing even at kHz repetition rates. This makes it a very useful Q-switch material, particularly for applications requiring high half-wave voltages [34]. The half-wave voltage for our BBO Q-switch was 5.1 kV at 1250 nm. The pulse timing unit supplies a bias current, which sends the voltage high in anticipation of the incoming pulse. It then switches down to zero for the duration of the pulse buildup in the cavity, and then back up to the half-wave voltage for switch-out. With a rise time of about 1 ns/kV, the driver can ramp-up to the half-wave voltage in 5 ns. Since the total cavity length is $\sim$1.5 m, the round trip time is 9 ns, or slightly less than twice the round trip time. It is then ensured that only one seed pulse is switched in, and all of the amplified pulse is switched out.

Of course, with a smaller gain, it is necessary to have the seeded pulse make more cavity round trips in order to have reasonable amplification. With increasing numbers of round trips, dispersion becomes a more prominent concern, particularly the high order dispersion that is not easily compensated in a grating compressor.

The oscillator pulse was first stretched using a grating stretcher, using a 1200 grooves/mm
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grating. Here, it is useful to refer to the grating dispersion equation

$$D = \frac{\partial \beta}{\partial \lambda} = \frac{\sin \alpha + \sin \beta}{\lambda \cos \beta},$$

(2.1)

where $D = \partial \beta/\partial \lambda$ is the angular dispersion, or change in diffraction angle per unit wavelength; $\alpha$ in the angle of incidence, and $\beta$ is the diffraction angle. The key point is that the grating dispersion is inversely proportional to the laser wavelength $\lambda$. Hence, we see that the primary difficulty with stretching and compressing IR pulses is that stretchers and compressors must be lengthened in order to compensate for the lower grating dispersion. The total length of the (folded) stretcher used here was about 2.5 m. The maximum output power obtained before compression was 300 mW at 1 kHz using 7 W of pump power. The overall efficiency of the system, $P_{\text{RGA}}/P_{\text{pump}}$, is 4%. This number is comparable to the results reported by other groups who have built similar systems [35, 36, 37]. The number of round trips required in this system is ~ 60 – 70, compared to ~ 20 – 30 for Ti:S RGA.

After compression, also using 1200 groove/mm gratings, the pulse widths were typically around 200 fs, although shorter pulses could be achieved using fewer round trips. Of course, there is an energy tradeoff involved here. Shorter pulses are possible, but only at the expense of having lower pulse energies due to the reduced number of passes through the amplifier. With ~ 40 round trips, 135 fs pulses were observed with 175 mW of total output power.

2.3 Phase matching and gain calculations OPAs pumped by Cr:Forsterite

2.3.1 Dispersion and pulse width considerations in OPAs

To date, the only reports of mid-IR generation using OPAs pumped by Cr:forsterite has been in the work of Rotermond and Petrov [38, 39]. Their scheme involved two OPA
stages instead of the single OPA method proposed in this work. They doubled a portion of the 1250 nm RGA light and used it to pump a BBO OPG stage. The OPG output was then mixed with the remainder of the 1250 nm fundamental beam in AgGaS$_2$ or HgGaS$_2$. The continuum-seeded method shown in Figure 2.3 is simpler and requires only one OPA stage. Also, with reference to Ti:S-pumped OPAs, gain bandwidths can be much larger when seeding with a continuum because continuum spectral bandwidths are normally much larger than those in OPGs/OPAs. For these reasons, the continuum-seeded approach was chosen for this work.

Thus far, little has been said about the temporal duration of the expected mid-IR pulses. The main considerations involved in minimizing pulse widths and temporal broadening in OPAs are 1) group velocity dispersion, 2) Poynting vector walk-off, and 3) intrinsic phase-matching bandwidths of the nonlinear crystals.

All of the schemes discussed to this point in this chapter use collinear phase matching geometries. That is, the pump, signal/seed, and idler beams all propagate in the same direction, with their $k$ vectors collinear. However, phase matching is still possible even if they are not mutually collinear. Naturally, such cases are known as non-collinear phase matching geometries. Of course, the three pulse width considerations listed above all depend critically on the chosen phase matching geometry. Some specifics as they pertain to the present work will be discussed further in the next section.

In order to achieve the best possible efficiency from a parametric process, the three interacting beams must be overlapped in time as well as space. Spatial overlap is typically quite easy to deal with by properly choosing the collimating and/or focusing optics to produce good mode matching in the nonlinear crystals. Achieving good temporal overlap is a far more difficult task, since each wavelength will have a different group velocity inside the crystal, causing them to temporally walk off from each other as they propagate. This can lead to temporal distortion of the output beams, power instabilities, and reduction of the small signal gain [40, 41].
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The concept of using a non-collinear geometry was first considered by diTrapani [42]. They showed that for a certain noncollinear angle $\alpha$, defined as the angle between the $\mathbf{k}$ vectors of the pump and seed beams, the group velocity dispersion between the pump and seed can be zero. In such a case, one expects a higher gain compared to the collinear geometry since there is longer temporal overlap between the pulses within the crystal. However, the beams are also walking off from each other spatially because their $\mathbf{k}$ vectors are not collinear. Energy walk-off can also occur because the Poynting vectors are not necessarily collinear. These walk-off angles depend on the beam polarizations, and therefore on the type of phase matching chosen (either Type I or Type II). In general, though, the choice of either Type I or Type II is a matter of maximizing the $d_{ef}$ [43], not minimizing the Poynting vector walk-off.

It is also advantageous to choose $\alpha$ such that the group velocity mismatch between the signal and idler is zero. In such a case, the best choice for $\alpha$ is the solution to the following equation [44]:

$$\left( \text{sin} (\alpha) \right)^2 = \frac{1 - \left( \frac{n_s}{n_i} \right)^2}{1 + \frac{2v_s n_s \lambda_s}{v_i n_i \lambda_i} + \left( \frac{n_s \lambda_s}{n_i \lambda_i} \right)^2},$$

(2.2)

where $\lambda_s, \lambda_i$ are the pump and signal wavelengths, with corresponding refractive indices $n_s, n_i$ and group velocities $v_s, v_i$.

2.3.2 Phase matching for AgGa$_2$ and KTA crystals

The group velocities of beams propagating through a dispersive nonlinear crystal depend on crystal orientation. The phase matching equations relate the group velocities and group refractive indices to the orientation of the nonlinear crystal. For a parametric process such as sum frequency or difference frequency generation, both energy and momentum will be conserved during the interaction. The necessary phase matching

---

1In this thesis, all equations are given in SI units
equations are [44]

\[
\frac{1}{\lambda_p} = \frac{1}{\lambda_s} + \frac{1}{\lambda_i}, \\
\frac{n_p}{\lambda_p} = \frac{n_s}{\lambda_s} + \frac{n_i}{\lambda_i},
\]

(2.3)  

(2.4)

where \(\lambda_p, \lambda_s, \lambda_i\) are the pump, signal and idler wavelength, while \(n_p, n_s, n_i\) are the corresponding refractive indices. The first equation is the conservation of energy equation, while the second is the conservation of momentum equation. The Seilmeier relations as well as the dependence of the refractive indices on crystal geometry were taken from standard reference texts [22, 45].

In Equation 2.4, all three beams are assumed to be collinear. For noncollinear geometries, where the angle between the \(k\) vectors of the pump and signal is \(\alpha\), the momentum equation is modified:

\[
\frac{n_p \cos(\alpha)}{\lambda_p} = \frac{n_s}{\lambda_s} + \frac{n_i}{\lambda_i} \sqrt{1 - \left(\frac{n_p \lambda_i \sin(\alpha)}{n_i \lambda_p}\right)^2}.
\]

(2.5)

Thus, once the type of phase matching is chosen (Type I or Type II), as well as \(\lambda_p\), the refractive indices \(n_p, n_s, n_i\) can be computed. Then, \(\alpha\) is calculated and full phase matching curves can be generated.

The phase matching curve tells us much of what we need to know about the possible gain bandwidth in the OPA. The bandwidth depends on the derivative, \(d\theta/d\lambda\), of the phase matching curve in the vicinity of the desired wavelength [22]. The “flatter” the curve, the greater the phase matching bandwidth. When comparing collinear and noncollinear phase matching curves, a few things become clear. First, for the collinear geometry, the derivative \(d\lambda/d\theta\) is always a maximum at twice the wavelength of the pump, i.e. degenerate phase matching conditions. For the noncollinear curve, the derivative reaches a maximum at a wavelength removed from this degeneracy point, and this wavelength depends on the choice of \(\alpha\). Intuitively speaking, we should expect the largest gain bandwidth for conditions that minimize the group velocity mismatch between signal
and idler beams. For $\alpha = 0$ (collinear phase matching), obviously the minimum group velocity mismatch (GVM) should occur for identical signal and idler wavelengths. This is certainly true for Type I phasematching, in which they will have the same polarization, and are in fact perfectly identical beams. As $\alpha$ increases, the GVM will no longer be zero for this degenerate wavelength, shifting instead to a different wavelength. Thus, the net effect of a noncollinear geometry is to shift the gain peak to an "effective" degeneracy wavelength, where "effective" indicates that the signal and idler beams are degenerate in their group velocities, not their wavelengths.

Figure 2.5 shows the collinear and noncollinear phase matching curves for Type I phase matching in AgGaS$_2$ with 1.25 $\mu$m pumping. The angle $\theta$ is the angle relative to the fundamental crystal z-axis, as it is typically defined in the literature. In the collinear curve, the $d\lambda/d\theta$ is infinite at $\theta = 44^\circ$, $\lambda = 2.5$ $\mu$m, as expected. The second derivative $d^2\lambda/d\theta^2$ is indicative of the gain bandwidth. In other words, the "flatness" at any point on the curve represents a phase matching tolerance – the flatter the curve, the greater the gain bandwidth at that point. The three noncollinear curves in Figure 2.5 were calculated for three values of $\alpha$, zero, 1.8 and 2.5 degrees. These desired values of $\alpha$ are calculated as a function of the signal-idler wavelengths using Equation 2.5. For a 2.7 $\mu$m idler, $\alpha$ was found to be 1.8$^\circ$, while for a 3.0 $\mu$m idler, $\alpha$ is 2.5$^\circ$.

For the curve with $\alpha = 1.8^\circ$, the effective degeneracy point occurs for idler wavelengths centred at 2.7 $\mu$m at a value of $\theta = 45.2^\circ$. For $\alpha = 2.5^\circ$, degeneracy shifts further to the red, toward idler wavelengths centred at 3.0 $\mu$m, at a value of $\theta = 46.6^\circ$, and the curve continues to flatten in the vicinity of 3.0 $\mu$m, which is expected to result in a larger gain bandwidth under those phase matching conditions.

BBO has been a popular choice of nonlinear crystal for many noncollinear OPA systems [46, 47, 48] and this is in part due to a fortunate and convenient similarity between the angle $\alpha$ used for optimal broadband visible outputs and the walk-off angle $\rho$ for those output wavelengths. The latter is the angle between the Poynting vector.
Figure 2.5: Collinear and noncollinear phase matching curves in Type I AgGaS$_2$ pumped at 1.25 $\mu$m. Blue curve: collinear phase matching. Black curve: noncollinear phase matching with $\alpha = 1.8^\circ$. Red curve: $\alpha = 2.5^\circ$.

and the propagation vector $\mathbf{k}$ of the pump beam. In BBO, with 400 nm pumping, Gale calculated $\alpha = 3.7^\circ$ while $\rho = 4.0^\circ$ [44]. Even though it might appear that the noncollinear geometry results in a short interaction length between the pump and signal beams, in actual fact the Poynting vector of the pump walks off nearly collinear with the $\mathbf{k}$ vector of the signal. This makes it possible to have efficient amplification over a large length of nonlinear crystal. For a 1.25 $\mu$m pump in AgGaS$_2$ with Type I phasematching, $\rho = 2.0^\circ$ for the pump, very close to the optimal $\alpha$'s discussed above. This indicates that efficient signal beam amplification should be possible.

The other remaining issue, as mentioned in Section 2.3.1, is the temporal walk-off between the pump, signal and idler beams. This is characterized by the quasi-static interaction length, $L_{qs}$, which for the case of the signal and pump beams, is given by

$$L_{qs} = \frac{\tau}{1/v_p - 1/v_s},$$

(2.6)
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where $\tau$ is the duration of the pulses and $v_p, v_s$ are the group velocities given by the associated phase matching conditions [45]. In the present case, for the pump and a 2.3 $\mu$m signal beam, this length is 1.26 mm. The group velocity of the idler, in the wavelength region above 2.7 $\mu$m, differs from that of the signal by only a few percent. For this reason, the OPA crystals used in this work were 1 mm in length.

2.4 Gain calculations for Cr:F-pumped OPAs

Huge gains are possible in parametric amplifiers, which offers considerable promise for scaling laser amplifiers to high powers in addition to their wide tunability [49]. In the small signal limit, the gain in a laser amplifier is [14, 49]

$$G = 1 + \left( \frac{g^2 (\sinh(\sqrt{g^2 - \Delta k^2}))^2}{g^2 - \Delta k^2} \right),$$  

(2.7)

where $g$ is the small signal gain and $\Delta k$ is the phase mismatch between the pump, signal and idler beams. The expression for $g$ is

$$g = 2\sqrt{2\pi} d_{eff} \sqrt{\frac{J}{\epsilon_0 n_p n_s n_i c}},$$  

(2.8)

where $J$ is the pump beam intensity, $c$ is the speed of light, and $\epsilon_0$ is the electrical permittivity of free space. For $\Delta k$ we have

$$\Delta k = 4\pi^2 \left( \frac{n_p}{\lambda_p} - \frac{n_s}{\lambda_s} - \frac{n_i}{\lambda_i} \right) \frac{L}{2},$$  

(2.9)

where $L$ is the crystal length. For perfect phase matching, $\Delta k = 0$ and gain is maximized. It has long been understood that this could allow for potentially huge OPA gains of $\sim 10^{11}$ or more [49, 50]. The dominant factor in the expression is the pump intensity, as the other factors are all material properties and are not scalable. So provided one could generate a pump beam with arbitrarily high peak intensities, the achievable parametric gain would appear to be limitless. Of course, this is only true in the small signal gain limit. Gains of $10^8$ have been observed [51] when seeding with extremely low power pulses.
Figure 2.6: Calculated gain bandwidth curves for Type I AgGaS$_2$ with 1.25 μm pump.

in the femtojoule range. A more typical single stage OPA gain (seeded by a white light continuum) is in the $10^3 - 10^4$ range [46, 47, 48, 52] – still considerable by any means.

Using the above expressions, the gain as a function of wavelength for Type I phase-matching in AgGaS$_2$ was calculated and appears in Figure 2.6. The crystal length was chosen to be 1 mm, since this is approximately the quasi-static interaction length for the pump and signal beams in the crystal [22].

In the calculation, the pump pulse was assumed to be 150 fs in duration, with pulse energy 50 μJ, and focused to a spot size of 400 μm in diameter. The choice of pump pulse parameters simply scales the peak gain, but otherwise they do not affect the shape of the gain curve in any way, since pump depletion was not taken into account in these calculations. For collinear gain, the gain peaks at 2.5 μm, as expected. The FWHM of the gain curve is approximately 500 nm. For the noncollinear cases, the peak gain shifts
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toward the red and is noticeably broadened. For $\alpha = 1.8^\circ$, the FWHM gain bandwidth approaches 600 nm, while for $\alpha = 2.5^\circ$, it is nearly 900 nm. A transform-limited Gaussian pulse with that bandwidth would be a sub-20 fs mid-IR pulse, which would be the shortest mid-IR pulses yet produced. Pulse durations in this range are essential for the study of pure liquid H$_2$O dynamics, as will be revealed in Chapters 5 and 6.

2.5 IR-OPA design and results

The OPA design appears in Figure 2.7. The amplified and compressed light from the RGA first strikes a beamsplitter, dividing the light into a pump arm and a seed arm. With 100 $\mu$J RGA pulses, an 80/20 beam splitter was used in order to provide enough energy to create the broadband seed continuum. Pinholes mark the beam path and can also be used for spatial filtering, which is particularly important for generating a stable continuum. The seed light is delayed by a retroreflecting delay line, and later focused using an $f = 5$ cm lens in order to produce the continuum (details to follow). The continuum is then collimated using a $f = 10$ cm lens that was mounted on a translation stage in order to allow for adjustment of the seed spot size in the OPA crystal. Two steering mirrors direct the seed toward the crystal and allow for adjustment of the noncollinear angle $\alpha$.

The pump passes through a $\lambda/2$ plate, which can be rotated to give zero or half-wave polarization rotation depending on the type of phase matching chosen for the OPA. It is then focused using a $f = 30$ cm lens into the OPA crystal. The spot size can be varied by translating the lens a few cm along the beam direction. Spot sizes as small as 200 $\mu$m were used, although 300 $\mu$m tended to be the standard size. It is interesting to note that we could, for prolonged periods of time, use such small spot sizes with intensities up to 100 GW/cm$^2$ without causing any damage to the OPA crystal. Damage thresholds for femtosecond pulses are not often cited in the literature. In particular, AgGaS$_2$ has a reputation of having a relatively low damage threshold [45], far below
what we observed. For many laser materials, the damage thresholds that are stated in the literature are typically measured using nanosecond or picosecond pulses. For femtosecond pulses, damage thresholds are expected to be considerably higher than they are for picosecond pulses. Those who are well-versed in the laser ablation arts are well-aware of this because the thermal damage threshold is proportional to the square root of the pulse width (see, for example, the patent by Neev et al. [53]). In addition, the transparency of the AgGaS₂ crystal was independent of the intensity, indicating that two-photon absorption was negligible.

Broadband IR continua have been produced by focusing tightly into nonlinear media using many types of laser systems. In particular, the operating specifications of the amplified NaCl colour-centre laser of Sucha [54] are quite similar to the Cr:F used here.
They used 150 fs, μJ-level pulses centred at 1.5 μm and produced continua from 400 nm - 3.5 μm in BaF₂. Nonlinear fibres have also been used extensively in continuum generation, mainly in conjunction with Ti:Sapphire lasers to produce visible and near-IR continua [55, 56](and references within). However, many centimetres or even metres of fibre may be needed to generate the necessary bandwidth, and therefore, dispersion of the propagating continuum becomes an significant issue. Also, phase and amplitude stability are known to be problems when using fibres to seed OPAs [57]. Generating the seed continuum in an optical window such as BaF₂ or Sapphire is simpler and easier to align than a fibre. Compared with Ti:S, the 1.25 μm wavelength of Cr:F is nearer to the zero-dispersion wavelength for many materials. It is believed that this is advantageous for minimizing the chirp of the continuum. This results in a larger effective length in the window over which the continuum can be generated [58].

Between 15 - 20 μJ were used to generate the continuum. This energy could be precisely controlled using a variable neutral density filter. No visible (by eye) or measurable continuum was observed using 2 mm thick borosilicate or BaF₂. With 3 mm BaF₂, continuum generation was barely at threshold. The greatest success, by far, was with the use of 1/8" (3.25 mm) Sapphire windows. The continuum was dispersed in a 0.24 m monochromator and detected using a liquid nitrogen cooled HgCdTe single channel detector. To aid in the detection of low intensity infrared signals, the beam was chopped and the MCT detector output was captured using a lock-in amplifier, as well as a boxcar integrator to discriminate against electrical noise and scattered light.

The measured white light spectrum appears in Figure 2.8. To the eye, colours throughout the visible spectrum could be seen and continuum could be measured down to 400 nm using a photomultiplier. This visible continuum was not quantified any further, in large part because the entire visible and IR continuum cannot be measured using the same detector. In order to measure the continuum intensity over four orders of magnitude, three different gain settings were used on the boxcar integrator. The intensities for each

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Figure 2.8: The infrared continuum generated in a 3.25 mm sapphire plate using ~15 $\mu$J of power from the Cr:F RGA. Its intensity drops off considerably above 1.5 $\mu$m, but still manages to reach as far as 2.5 $\mu$m. Light throughout the visible spectrum were observed, but only the wavelengths above 1.3 $\mu$m were measured here, since no single detector can span the entire visible and mid-IR wavelength range. The different colours shown correspond to data taken at three separate gain settings with the boxcar integrator.

Gain setting were then matched in order to produce the continuous tri-coloured curve in the figure.

The main purpose behind the data in Figure 2.8 was to determine the spectral power density in the continuum in comparison with the 1.25 $\mu$m fundamental light used to produce it. For visible white-light seeded OPAs, this power density tends to be about an order of magnitude less than the fundamental (800 nm) light [47, 52]. In the present data, the spectral density falls off sharply with increasing wavelength, and above 2.0 $\mu$m it is about three orders of magnitude lower than the 1.25 $\mu$m fundamental. From this result, the spectral power density near 2.0 $\mu$m can estimated as 100 pJ/nm.

Spectra of the mid-IR signal and idler outputs appear in Figure 2.9. The pump
pulses were from 50 - 80 µJ in energy, with pulse widths of ~ 200 fs. Ge windows with cutoffs below 2.0 µm were used to filter out any stray 1.25 µm pump light as well as the IR continuum. The noncollinear angle was set so that α = 2.0°. The idler beam was spatially separated from the signal and the beams were isolated using a series of irises. To tune the spectra, a centre wavelength for the idler was chosen, followed by adjustment of the angle θ in order to maximize the gain. For idler wavelengths above 3.4 µm, the signal beam is not shown since it is cutoff by the Ge filter. The calculated and observed phase matching angles θ are in reasonable agreement, with discrepancies of less than three degrees. The idler spectra are about 400 nm broad (FWHM), which is anticipated when θ is set far from the effective degeneracy point in the noncollinear
Figure 2.10: Comparison of calculated and observed IR-OPA spectra. All curves have been normalized for the basis of comparison. Red curve: observed IR-OPA spectrum for $\alpha \cong 2.0^\circ$, $\theta = 49^\circ$. Black curve: calculated noncollinear gain for $\alpha = 1.8^\circ$, $\theta = 45.2^\circ$. Blue curve: calculated noncollinear gain for $\alpha = 2.5^\circ$, $\theta = 46.6^\circ$. The observed gain bandwidth is actually 20% larger than the largest calculated gain bandwidth.

In Figure 2.10, this large observed gain bandwidth is compared with the calculated profiles. The long tail on the red edge of the observed spectrum qualitatively matches that of the calculated plot for $\alpha = 2.5^\circ$. Somewhat surprisingly, the observed bandwidth exceeds the calculated bandwidth by 20%. Precise tuning of the centre wavelength was difficult because of the extreme sensitivity of the observed spectra with respect to $\alpha$ [60].

In more practical terms, very small adjustments of the seed beam steering mirrors could...
result in large changes to the observed spectra. Nonetheless, once aligned, the spectrum was quite stable and the power fluctuations were \( \sim 5\% \), approximately mimicking the power stability of the RGA pulses. Gains of \( \sim 10^2 \) were measured, smaller than the \( 10^3 - 10^4 \) range of many visible OPAs [47, 52]. By adding a second pass to the OPA, a further gain of three was observed, although the proximity of the optics could not allow for space to refocus the signal or idler beams and optimize the mode matching on the second pass. The reasons for the lower than expected gain are not fully understood at this time. The energies of the resultant nJ-level pulses were too small for performing a FROG characterization.

Attempts were also made using Type II KTA as the OPA crystal. KTA is a commonly used nonlinear material for wavelengths up to 4.0 \( \mu \text{m} \), with a higher damage threshold than that of AgGaS\(_2\) [61]. No mid-IR output could be successfully measured with KTA as the OPA crystal, likely because its \( d_{\text{eff}} \) for KTA is one-third that of AgGaS\(_2\).

Future work must focus on increasing the seed energy within the continuum. Because the desired seed wavelengths are far to the red of the fundamental wavelength of 1.25 \( \mu \text{m} \), the spectral power density of the IR continuum is at least two orders of magnitude smaller than it is with visible white light-seeded OPAs. The most promising solution is to generate the continuum using a single mode, air-guided fibre or microstructured fibre [55, 62, 63]. Using these types of fibres, efficient IR and visible supercontinuum generation has been demonstrated, and the zero dispersion wavelengths of the fibres can be easily tailored for 1.25 \( \mu \text{m} \) wavelengths. Nonetheless, continuum-seeded OPAs pumped at 1.25 \( \mu \text{m} \) are capable of producing mid-IR pulses with tremendously wide spectral bandwidths after amplification. Up to 1700 cm\(^{-1}\) bandwidths were observed at a central wavelength of 2.7 \( \mu \text{m} \). These spectral pulse widths correspond to a 14 fs transform-limited infrared pulse, which would be the shortest pulses in this wavelength range by at least a factor of three.

This IR laser system serves as the base technology for our high powered femtosecond
IR laser development. During the course of these studies, a decision was made to pursue an Optical Parametric Chirped Pulse Amplification (OPCPA) scheme in conjunction with the work described in this chapter. The OPCPA concept shows strong potential for overcoming the low gain problems in Cr:forsterite with respect to achieving higher OPA pump powers. The OPCPA system is nearing completion with output energies in the mJ range in the near-IR at 1.5 μm. The above study laid the foundation for this laser source development. The 2D-IR experiments that are described in the remainder of this thesis were conducted in parallel to this laser source development work.
Chapter 3

Multidimensional IR spectroscopy

3.1 Photon Echoes

Photon echo spectroscopy is the optical analogue of the spin echo spectroscopy that is used in Nuclear Magnetic Resonance (NMR). At present, NMR is a highly developed field that has been a valuable and successful method for inferring the structures and millisecond dynamics of complicated biomolecules by probing couplings between the spins of nuclei [64]. Detailed treatments of photon echo have been addressed elsewhere, such as in Allen and Eberly’s classic text [65]. More recently, comparisons between optical and NMR spectroscopy in one and two dimensions were extensively covered by Keusters et al. [66]. Briefly, photon echo is used to distinguish between inhomogeneous and homogeneous broadening processes. The former type is due to the presence of different static local environments or substructures within the sample. Conversely, homogeneous broadening processes represent the dynamics of interest that are typically masked beneath the inhomogeneously broadened spectrum. Information about intermolecular coupling, spectral diffusion, and energy transfer between molecules are all contained in the homogeneous spectral features.

In a three-pulse echo sequence in NMR, the spin system (analogue of the polarization
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system in the optical regime) coherently evolves into a non-equilibrium state in the time interval \( \tau \) between the first two excitation pulses (see Figure 3.1). In NMR, this is called the preparation period. Between the second and third pulses (a time interval \( T \)), the prepared state evolves according to the system Hamiltonian, with dynamical processes (intermolecular coupling, population relaxation, etc) taking effect on the system during this time. Following the third excitation pulse, a rephasing of the spin/polarization can occur. When the second and third pulses are overlapped in time, the nonlinear signal generated as a function of \( \tau \) is called the photon echo (analogous to the NMR spin echo). The decay of the echo signal provides information about the coherent polarization produced in the sample following excitation. The interval between the third pulse and the echo signal is known as the echo peak shift, which is notable because it can be directly related to the frequency-frequency correlation function

\[
C(t) = \left< \delta \omega(t) \delta \omega(0) \right>,
\]

where \( \delta \omega \) is the shift in the time-dependent vibrational transition frequency from its average value \([67, 68, 69]\). Both the static and dynamic information about the system are completely defined by \( C(t) \). For a completely inhomogeneously broadened ensemble, \( \delta \omega \) does not vary with time, all the spins completely rephase at a time \( t = \tau \) following the third excitation pulse, and the signal decays with a \( T_2/4 \) time constant (where \( T_2 \) is the pure dephasing time). For a completely homogeneously broadened ensemble, no rephasing can take place and the detected signal peaks at \( t = 0 \) following the third excitation pulse, and decays with a time constant \( T_2/2 \) \([70]\). Consequently, for ensembles with both types of broadening, the echo will peak at a time \( 0 < t < \tau \). Thus, the degree of homogeneous and inhomogeneous broadening in the system at any value of the \( T \) can be inferred by measuring the temporal position of the echo peak with respect to \( t = 0 \). In this way, information about the frequency-frequency correlation function \( C(t) \) can be inferred from an echo peak shift measurement.

The recent development of femtosecond mid-infrared laser sources has allowed the principles used in NMR to be applied to vibrational excitations of molecules \([71, 72]\).
The femtosecond time resolution that is accessible with ultrafast sources are orders of magnitude better than what is achievable with NMR spectroscopy. Thus, an understanding of the picosecond and even femtosecond vibrational and orientational motions of molecules becomes achievable.

Figure 3.1: The pulse sequence used for three-pulse echo experiments. The two pump beams $k_1, k_2$ are separated by the coherence time $\tau$, while the second pump and probe beam $k_2, k_3$ are separated by the population time $T$. The fourth beam is the weak reference pulse $k_{\text{ref}}$, which is necessary for heterodyne detection. The coherence time $\tau$ and population time $T$ are analogous to the same terms used in NMR spectroscopy.

Thus, by obtaining information about the decay of the coherent polarization in the system, the types of broadening mechanisms present and the dephasing times can be found. All of this can be done by measuring intensities of the two or three pulse echoes using a single photodiode. However, by measuring only the intensity of the echo signal, information is lost. A more complete understanding of the system dynamics comes from characterizing the amplitude and phase of the echo, or equivalently, its absorptive and dispersive components. Thus, a temporal characterization of the echo at a chosen value of $T$, plotted as a function of the coherence time $\tau$, would spread the echo signal into two time dimensions. For each $\tau$, the shape of the generated echo field depends on the vibrational coherences that contribute to it. The frequency domain representation of the multidimensional time echo therefore spreads the nonlinear vibrational response of the
system into two frequency dimensions. This 2D-IR echo is the analogue of 2D-NMR echo spectroscopy. In turn, an optical pulse sequence, analogous to an RF pulse sequence as described above, is shown in Figure 3.1.

A schematic picture of a model 2D-IR spectrum appears in Figure 3.2. The IR absorption spectrum of the model system is shown along the edges of the 2D diagram and consists of two vibrational transitions \(a\) and \(b\) centred at frequencies \(\nu_a\) and \(\nu_b\) that are well separated in frequency. The on-diagonal peaks, shown in grey, represent fundamental transitions between the \(\nu = 0\) and \(\nu = 1\) vibrational levels of each transition. In the presence of coupling between vibrations \(a\) and \(b\), the excitation can transfer from one vibrator to another. This manifests itself via off-diagonal peaks, which are coloured red in the figure. In other words, one excites at a frequency \(\nu_a\) and detects a component of the echo signal at a different frequency \(\nu_b\), because the coupling between the two transitions allows for vibrational energy transfer between them. Finally, off-diagonal peaks shown in blue represent excited state absorption transitions between the \(\nu = 1\) and \(\nu = 2\) vibrational levels of each transition. This peak carries the opposite sign of the fundamental (\(\nu = 0 \rightarrow \nu = 1\)) on-diagonal peaks, which is clear from the \(\pi\) phase difference between the Feynman paths that correspond to the pulse interactions that are represented by the two sets of peaks [72]. Clearly, these excited state absorption peaks can exist in the 2D spectrum even in the absence of coupling between \(a\) and \(b\), for they represent excitation at \(\nu_{a,b}\) and detection of a component of the echo signal at \(\nu_{a,b} - \Delta_{a,b}\), where \(\Delta_{a,b}\) is the anharmonicity of the vibrator.

Furthermore, the shapes of the peaks in the 2D spectrum are indicative of the degree of homogeneous and inhomogeneous broadening. Their ellipticities are indicative of the degree of inhomogeneity of the observed transition. That is, the ratio of the diagonal width (along the line \(\nu_1 = \nu_3\)) and the anti-diagonal width (along \(\nu_1 = -\nu_3\)) of the peak is related to the ratio of the inhomogeneous to the homogeneous linewidths [73, 74]. Equivalently, elliptical (as opposed to circular) peaks in the 2D spectrum are indicative
Figure 3.2: Schematic plot of a model 2D-IR spectrum. The on-diagonal peaks represent fundamental transitions between $\nu = 0$ and $\nu = 1$ vibrational levels. The blue off-diagonal peaks represent excited state absorption from the $\nu = 1$ to $\nu = 2$ level. The red off-diagonal peaks indicate the presence of coupling between the two vibrators $a$ and $b$. The shapes of the peaks are indicative of the degree of homogeneous and inhomogeneous broadening.

of frequency correlations between subensembles beneath the linear IR spectrum, which can be characterized by the frequency correlation function $C(t)$.

### 3.2 Measuring the 2D-IR spectra

A typical three-pulse sequence is shown in Figure 3.1. The first two excitation pulses, $k_1$ and $k_2$ are separated by the coherence time $\tau$. The second and third excitation pulses $k_2$ and $k_3$ are separated by the population time $T$. In one possible three-pulse echo measurement, $T$ is held constant, $\tau$ is scanned and the echo signal is measured as a function of $t$. With heterodyne detection, the signals $\text{Re}(E(\tau,T,t))$ and $\text{Im}(E(\tau,T,t))$ –
the real and imaginary parts of the electric field of the echo – can be extracted \(^1\). This requires the local oscillator (LO) to be overlapped in time with the echo signal. The heterodyned signal is then measured as a function of the time delay \(t\) between the echo signal and the LO. Fourier transforming these signals with respect to \(\tau\) and \(t\) produces a complex 2D-IR spectrum that is analogous to the 2D-NMR spectrum.

The echo signal can be directly detected using a photodiode. This is called homodyne detection. However, heterodyne detection, involving interference of the echo signal with a local reference pulse, offers several distinct advantages. Homodyne detected signals are recorded as a function of intensity only. Thus, information about the echo signal is lost because the amplitude and phase of its electric field are not characterized with this type of measurement. With heterodyne detection, the signal \(E_{\text{sig}}\) is interfered with a weak reference pulse \(E_{\text{ref}}\) so that the total detected signal is

\[
I_{\text{het}} = |E_{\text{ref}} + E_{\text{sig}}(t, T, \tau)|^2, \\
I_{\text{het}} = |E_{\text{ref}}\exp(i(\omega_{\text{ref}} t + \phi_{\text{ref}})) + |E_{\text{sig}}(t, T, \tau)|\exp(i(\omega_{\text{sig}} t + \phi_{\text{sig}}))|^2, \quad (3.1)
\]

where \(E_{\text{ref}}\) and \(E_{\text{sig}}\) are the reference and signal fields (along with their respective field amplitudes) and \(\phi_{\text{ref}}\) and \(\phi_{\text{sig}}\) are their respective phases. In a practical sense, the frequencies \(\omega_{\text{ref}}\) and \(\omega_{\text{sig}}\) are not monochromatic, rather, they are frequency distributions. Of course, the distribution \(\omega_{\text{sig}}\) will, in general, also depend on the values of the time variables \(t, T, \tau\). The above equation simplifies to:

\[
I_{\text{het}} = |E_{\text{ref}}|^2 + |E_{\text{sig}}(t, T, \tau)|^2 + 2\cos|E_{\text{ref}}||E_{\text{sig}}|(t, T, \tau)\cos((\omega_{\text{ref}} - \omega_{\text{sig}})t + (\phi_{\text{ref}} - \phi_{\text{sig}})). \quad (3.2)
\]

\(^1\)In NMR terminology, due to phase conventions, the real part of the echo signal corresponds to the absorptive component, and the imaginary part to the dispersive component of the echo. To avoid confusion, the physically descriptive terms “dispersive” and “absorptive” will be used in this thesis.
Since $|E_{ref}| \gg |E_{sig}|$, then the $|E_{sig}|^2$ term is negligible, and the $|E_{ref}|^2$ term is a time-independent background that can be subtracted off from the heterodyne signal. The remaining term is dependent on the electric fields and their phases. It is proportional to $|E_{ref}|$, which means the detected signal can be scaled with the intensity of the reference, provided the reference remains weak enough to not disturb the sample and its noise variations remain small compared to that of the signal field amplitude. Finally, $|E_{ref}|$ can be divided out to give $E_{sig}(t, T, \tau)$. This linearization of the signal detection greatly increases the sensitivity and available dynamic range compared with homodyne detection methods [72]. The other essential feature of heterodyne detection is that it enables the measurement of phase differences between signal and reference beams, which is required in order to separate out the dispersive and absorptive contributions to the signal. In addition, in analogy to linear spectroscopy, the dispersive contribution is quite broad and typically masks the couplings of interest. By separating the absorptive and dispersive components of the signal field, the 2D spectrum sharpens up considerably in comparison with the homodyne detected field, as first pointed out by Hybl et al. [75]. This feature is essential to 2D-NMR, and is equally important in 2D-IR.

The electric field of the echo pulse is a function of the time variables $\tau$, $T$, and $t$, which were defined in Figure 3.1. The echo signal propagates in the phase-matched echo direction $k_2 - k_1 + k_3$. After subtracting the constant background and dividing by $E_{ref}$, the remaining heterodyne signal $E_{sig}(t, T, \tau)$ – provided its phase is known – is a measure of the real part of the echo electric field. The phasing procedure will be discussed in Section 3.3. This generated photon echo field results from the response of the sample to the three laser fields $(k_1, k_2, k_3)$. The nonlinear interactions that contribute to the response function of the sample are usually depicted using Feynman diagrams. The response function of the sample will depend on the dynamical contributions from all applicable Feynman diagrams, as well as the transition dipole moments associated with these diagrams. In addition, the relative strengths of each nonlinear interaction can also
depend on the polarizations of the excitation pulses.

The detected third-order polarization can be written as \[ \text{[76, 70, 77]} \]

\[
P^{(3)}(t) = \int_0^\infty dt' \int_0^\infty dT \int_0^\infty d\tau E_1(r_1, t-\tau-T-t')E_2(r_2, t-T-t')E_3(r_3, t-t') \sum_i R_i(\tau, T, t),
\]

(3.3)

where the fields \( E(\mathbf{r}) \) represent the (time ordered) excitation pulses, and \( \sum_i R_i(\tau, T, t) \) entails the sum of the response functions associated with the Feynman processes that contribute to the observed signal. For example, here are two possible contributions to \( R_i(\tau, T, t) \):

\[
R_i(\tau, T, t) = i e^{i\omega_{\tau}t} \langle 0_i | b_i c_i d_i | 0 \rangle (F(0i|ii|i0) - F(0i|ii|i + i, i)e^{i\Delta t}) e^{-i\omega_{\tau}t}.
\]

(3.4)

These two terms in \( R_i(\tau, T, t) \) correspond to the double-sided Feynman diagrams in Figure 3.3 [78], illustrating the evolution of the density matrix of the system.

![Figure 3.3: Two sample Feynman diagrams that can contribute to the 2D-IR spectrum (see text for more detail).](image)

The corresponding factors \( (F(0i|jk|lm)) \) contain the dynamical contributions to the Feynman diagrams. They can be calculated, for example, by assuming a Bloch or Kubo
model to describe the interactions of the electric field with the system, and the system with the surrounding bath \[79\]. The expression \( \langle a_i b_j c_k d_l \rangle \) depends on the polarizations of the IR pulses, as well as the time-dependent orientation of the excited dipoles. The 2D Fourier transform of the field generated by \( P^{(3)} \) produces the 2D-IR spectrum.

In the examples shown in Figure 3.3, each field interacts with a single transition. The diagram on the left corresponds to fundamental transitions, depicted by the grey peaks in Figure 3.2. The system responds with a frequency \(-\omega_i\) during the time interval \(\tau\), and a frequency \(\omega_i\) during the time interval \(t\). The diagram on the right corresponds to excited state absorption, depicted by the blue peaks in Figure 3.2. Here, the system response during \(t\) is a shifted toward the red due to the anharmonicity, at a frequency \(\omega_i - \Delta_i\). As mentioned in Section 3.1, these terms carry opposite signs because of the \(\pi\) phase difference between their respective Feynman paths. Pictorially, this is easy to visualize by the number of interactions from the right in the corresponding Feynman diagrams. The sign convention is given as \((-1)^n\), where \(n\) is the number of interactions from the right.

Thus, the echo field is generated by the nonlinear polarization \( P^{(3)}(t) \), given the appropriate system response \( R_i(\tau, T, t) \). To obtain the 2D-IR spectrum, two of the time variables are scanned; for instance, \(\tau\) and \(t\) can be scanned while holding \(T\) constant. Then, a Fourier transform of \( \text{Re}[E_{\text{sig}}(t, T, \tau)] \) along \(t\) and \(\tau\) will yield the complex 2D-IR spectrum. The absorptive and dispersive components are extracted by determining the phase of the 2D-IR spectrum, which will be explained in the next section. Consistent with the nomenclature in the 2D spectroscopy literature \[75, 80\], the 2D-IR spectrum is denoted \( S(\nu_3, \nu_1, T) \), where \(\nu_3\) is the frequency domain variable associated with \(t\), and \(\nu_1\) is the frequency that is associated with \(\tau\). For a more extensive discussion of the theory behind 2D-IR, refer to the work of Zanni et al. \[78\], Ge et al. \[79\], and Zhang et al. \[81\].
3.3 Echo detection using spectral interferometry

Another method of acquiring the same information is to use spectral interferometry [82, 83]. Scanning the time delay $t$ requires scanning the delay of the reference pulse. In contrast, with spectral interferometry, the time delay between the echo signal and the reference is fixed at a value $\Delta t$. The two beams are then dispersed in a monochrometer, where the beams interfere in the spectral domain. Analogous to the case of time domain heterodyned detection, the detected signal consists of a constant background plus a spectral interference term. The latter term is the product of the reference spectrum and the echo spectrum, and is modulated by the frequency $1/\Delta t$. The envelope of this spectral trace is the desired photon echo signal as a function of frequency. Thus, detecting the signal in the frequency domain using spectral interferometry obviates the need to perform a Fourier transform over a second time variable. Instead, the monochrometer performs the Fourier transform over $T$ and the frequency $\nu_3$ is detected directly. The coherence time $\tau$ is scanned, with a spectral interferogram measured for each value of $\tau$. Finally, the function $E_{\text{sig}}(\nu_1, \tau, T)$ (where $T$ is once again held constant) is Fourier transformed along $\tau$ to give the 2D spectrum, which can be denoted as follows [80, 76]:

$$S(\nu_3, \nu_1, T) = i \times \text{sign}(\nu_3) \int_0^\infty P(\nu_3, \tau, T) \exp(2\pi i \nu_1 \tau) d\tau,$$

(3.5)

where the third order polarization $P$ is related to the signal field in that

$$i \times \text{sign}(\nu_3) P(\nu_3, \tau, T) \propto E(\nu_3, \tau, T)/\nu_3.$$

A sample spectral interferogram appears in Figure 3.4. This is the echo signal obtained at $\tau = 0$ fs in a 0.2 OD sample of liquid H$_2$O, from data that will be presented in Chapter 6. There is much more to be said about the water echo experiment in later chapters. But for the moment, Figure 3.4 conveniently demonstrates what a typical spectral interferogram looks like. The $|E_{\text{ref}}|^2$ background has been subtracted off, along with any scatter from the pumps or probe (via chopping). This spectrally modulated signal $S(\tau_0, \nu_3)$ is Fourier transformed with respect to $\nu_3$. Then, the negative and DC
Figure 3.4: Sample fringe pattern obtained using spectral interferometry. The figure shows the echo signal at $\tau = 0$ fs in a 0.2 OD liquid H$_2$O sample. The fringe frequency is $1/\Delta t$, determined by the delay $\Delta t$ between the signal and reference pulses.

frequency component can removed by multiplying by a filtering function such as the Heaviside function $\Theta(t)$. Dividing the result by $|E_{\text{ref}}|$ and Fourier transforming back into the frequency domain gives the complex field $E_{\text{sig}}(\tau_0, \nu_3)$ for the chosen slice:

$$E_{\text{sig}}(\tau_0, \nu_3) = \frac{F[\Theta(t)F^{-1}S(\tau_0, \nu_3)]exp(-2\pi i\nu_3 t)}{|E_{\text{ref}}|},$$

where $F$ denotes a Fourier transform between the time variable $t$ and the frequency variable $\nu_3$. This calculation, performed over all values of the scanned time variable $\tau$, gives the full complex 2D-IR spectrum once Fourier transformed over $\tau$.

The final step is to phase the 2D-IR spectrum. The fitting procedure is the same as the one that is used in 2D visible spectroscopy [75, 80]. The 2D spectrum $S(\nu_3, \nu_1, T)$ is multiplied by a phase factor $e^{i\phi}$. The real part of the projection of this expression onto the $\nu_3$ axis is then computed. The projection is then fitted to the frequency-resolved pump-probe spectrum taken at the same value of $T$. This pump-probe spectrum does
not depend on the relative phase between the excitation pulses and therefore a unique fit to the phase factor $\phi$ can be found. In this manner, we are able to separate the absorptive and dispersive components of the echo by properly identifying the phase of the echo signal.

Detection of the spectral interference pattern is possible using a single channel IR detector. The monochromator slit then determines the frequency resolution of the detected signal. Nonetheless, in practical experimental terms, the frequency $\nu_3$ must be scanned, just as the time delay $t$ is scanned when employing ordinary heterodyne detection using a single detector. Spectral interferometry becomes a more useful and powerful method if the spectral fringes are detected using a linear IR array. In this case, large chunks of the spectrum are detected at once, greatly reducing the time needed for scanning. Depending on the detector geometry and the frequency range to be scanned, it is possible to capture the entire spectrum at once, which has indeed been accomplished in visible echo spectroscopy [75, 80].

Using an array detector, the pixel width assumes the role of the monochromator slit and determines the frequency resolution of the detected signal. The present work used a 16-element LN$_2$-cooled MCT array detector made by Infrared Associates. Each pixel was 0.5 mm pixel wide, with 0.1 mm gaps between each pixel. Together with the 300 grooves/mm grating used in the monochromator, this corresponded to a frequency resolution of 10 cm$^{-1}$/pixel.

More advanced techniques have been developed with the goal of bringing the analogues of the techniques of 2D-NMR spectroscopy into 2D-IR spectroscopy. Keusters et al. [66] extensively compared the parallels between the two disciplines with the stated aim of incorporating phase techniques into the optical domain. By controlling the phases of the excitation pulses, they showed that 2D optical spectroscopies can select for specific coherence pathways, hereby isolating certain peaks in the 2D spectrum while eliminating others completely. This is the optical analogue of phase cycling in NMR. Zanni
et al. demonstrated that varying the polarization conditions of the excitation pulses could discriminate against on-diagonal peaks in the 2D spectrum while selecting for the cross peaks [71]. This method was successfully executed in the present work and will be discussed in further detail in Section 6.1.

To summarize, 2D-IR echo spectroscopy spreads conventional photon echo signals into two frequency dimensions and is the optical analogue of 2D-NMR. The 2D-IR spectrum is obtained by fully characterizing the spectral amplitude and phase of the photon echo signal. The shapes and spectral positions of the peaks contain information about the intra and intermolecular couplings in the sample as well as the degree of homogeneous and inhomogeneous broadening that is present in the system of interest. This information is crucial for extracting of the many body potential of liquid water using these ultrafast IR spectroscopies. The following chapter will describe the experimental design used to implement this 2D-IR technique.
Chapter 4

Multidimensional IR Spectroscopy
Using Diffractive Optics

4.1 Diffractive optics: an introduction

Practical, everyday laser usage is far more difficult with infrared beams than with visible beams. Tasks such as beam steering, collimation, and overlap - all of which are fairly simple tasks using visible beams - become challenging in the infrared. Furthermore, with IR wavelengths greater than 1.5 μm, the challenge is increased because the beams are no longer detectable using phosphor cards and handheld phosphor-based IR viewers. For a third-order echo experiment (requiring at least three beams), all beams must be generated from one main beam and subsequently re-overlapped both spatially and temporally. Ease of alignment and day-to-day alignment stability is a profoundly crucial consideration in the design of any infrared spectroscopy experiment.

Another challenge is ensuring phase stability between all the pulses. Heterodyne detection requires phase locked pulse sequences with minimal long-term drift. During the run time of any phase-sensitive experiment, we would expect that the phase drift of any pulse should be far less than its wavelength in order to preserve phase relations between
Chapter 4. Multidimensional IR Spectroscopy Using Diffractive Optics

all pulses. In this respect, infrared spectroscopy has an intrinsic advantage over visible spectroscopy because longer wavelengths will lead to larger tolerances in the required stability of the optical components. In the visible, both active phase locking via feedback loops [84, 85] and passive phase-locking using diffractive optics [86] have been demonstrated. The latter is by far the simpler method. The diffractive optic (DO) locks the phases of all pulses that are generated from it. In contrast to a beam pattern created using a succession of beamsplitters, if all beams strike the same optics following generation at the DO, then the subsequent phase variations will be the same for each beam. Furthermore, since the beam pattern is created at the DO, beam alignment (particularly in the infrared) is greatly simplified. In past implementations of the diffractive optics technique [87, 88, 89, 90], a transmissive optic was used, which was usually fabricated from fused silica. Unfortunately, the most common forms of fused silica are not transparent in the mid-IR. To circumvent the problem, we opted for a reflective DO. The DO, designed by INO (Rimouski, Quebec) featured six diffraction gratings on a 1” diameter fused silica substrate, which was gold-coated for maximum reflectivity. The gratings were optimized to give 35% reflectivity into both the +1 and -1 diffraction order. The first order diffraction angles for three of the gratings were ±1.1, 2.2 and 4.4 degrees at 3.0 μm wavelengths. The diffraction angles for the other three gratings were identical, except optimized for 1.25 μm wavelengths. This latter trio was intended for alignment purposes. That is, the fundamental light from the Cr:F laser (which can be seen using viewers or phosphor cards) could first be used to align the experimental setup. Following this, the DO could be shifted in order to switch to the grating with the same diffraction angle for the experimental 3.0 μm wavelength. Fortuitously, this wavelength is also nearly twice that of common alignment tools such as red HeNe lasers and AlGaInP laser diodes. This increases the number of laser alignment options, although in the case of these ~ 630—670 nm red wavelengths, the diffraction angle will be about half that at 1.25 μm, so alignment must be done using a grating with half the diffraction angle.
4.2 Diffractive-optic based IR setup for infrared spectroscopy

The experiments described in the remainder of this thesis were carried out in collaboration with the research group of Erik Nibbering and Thomas Elsässer at the Max Born Institut für Kurzzeitspektroskopie und Nichtlineare Optik, in Berlin, Germany. Mid-IR pulses were generated using the cascaded OPA method that was described in Section 2.1. A Ti:S RGA was used to pump a white light-seeded near IR OPA, followed by DFG between the OPA signal and idler in order to produce mid-IR wavelengths. The Spectra Physics Tsunami oscillator was pumped with 4.5 W from a SP Millenia green laser. The oscillator produced > 400 nm of mode-locked output in a 60 fs pulse. The RGA was pumped by the 5W, 1 kHz output of a SP Merlin – a flashlamp-pumped, intracavity doubled Nd:YAG laser. The pulse stretcher, compressor, and RGA cavity are all contained within a SP Spitfire RGA package. Outputs before the compressor were typically 1.3 – 1.4 W, and 0.9 – 1.0 W after compression. The pulse width was measured to be < 100 fs using a BBO-based SHG autocorrelator. In order to minimize pulse-to-pulse power stability, temperature stability (particularly crucial for all nonlinear crystals), and fluctuations due to air currents, great care was taken in covering all beam paths using tubes and/or lidded boxes.

The two-stage OPA design has been described in the paper by Hamm et al. [41], but in preparation for these IR water echo experiments, the original OPA design was altered in order to boost the output power. In the new design, the signal and idler beams are double-passed in the first BBO OPA stage. This creates two pre-amplifier stages (instead of one) before the power amplifier stage in the second BBO crystal. Using beamsplitters, the ~ 900 µJ, 800 nm pump pulses are split into three parts. About 5% is used for the first OPA stage, 20% for the second, and 75% for the third. The maximum near-IR output (total energy of the signal and idler pulses) after the power amplifier stage was 220

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In the DFG stage, around 20% of this energy is lost to the dichroic mirror that splits the signal and idler beams. The timing between the two beams is set via a translation stage in the signal arm, and both beams are focused to ~ 500 μm spot sizes into a Type I AgGaS$_2$ crystal that is 0.75 mm in length. This produces mid-IR pulses close at the 10 μJ level. Longer crystals that were 1.0 mm or longer could generate higher pulse energies, but the pulse spectra were irregularly shaped due to temporal walkoff between the pump and near-IR pulses.

For the best stability with 3 μm pulses, 150 μJ (total energy of signal and idler) were incident on the DFG crystal. This resulted in 3 μm output pulses with 8.5 μJ energies. This corresponds to a 5.7% power efficiency and 22% quantum efficiency, which is comparable to what is observed by other groups using similar cascaded OPA schemes based on Ti:S amplifiers and AgGaS$_2$ crystals [17, 18].

The complete DO-based setup appears in Figure 4.1. The incoming IR light first strikes a 50/50 beamsplitter. The reflected portion creates the two pump beams, while the transmitted portion creates the probe and reference. The probe/reference beams are delayed by a time $t_{13}$ by the first translation stage. Both pairs of beams are then focused onto the reflective DO via a 90° off-axis parabolic mirror (OAPM) with a working focal length of 10 cm. The 90° off-axis mirrors allow for maximum separation of the beams, which is crucial when using such short working distances. Besides minimizing the pointing instabilities via the short paths, such short focal lengths are necessary in mid-IR spectroscopy because the focal spot sizes are proportional to the wavelength. In a third order experiment, since the intensity of the generated nonlinear signal varies as the third power of the excitation intensity, then it is also clear that using the shortest possible focal lengths and minimizing the beam spot sizes is essential. Unfortunately, there is an inherent handicap in using IR wavelengths because the minimum spot size is proportional to the wavelength. In this DO setup, a collimated 3.0 μm beam that was 8 mm in diameter was focused down to a ~ 150 μm spot when focused by a 10 cm focal
Figure 4.1: Diffractive optics-based photon echo setup for the infrared. Pulses from the mid-IR OPA are split into two at a beam splitter, and one is given a variable delay $t_{13}$ using a retroreflector on a translation stage. Both beams are focused onto a reflective diffractive optic at near normal incidence using an off-axis parabolic mirror. The diffractive optic is optimized to diffract 70% of the intensity of each beam into the ±1 diffraction orders. The resulting four beams lie at the corners of a square, forming a "boxcar" pattern. The bottom two beams are delayed by a time $\tau$, giving the pulse sequence shown in Figure 3.1.

Each beam is focused onto the diffractive optic with a spot size of about 150 $\mu$m. The four beams are collimated using another OAPM. The four pulses are labelled $k_1, k_2, k_3, k_{\text{ref}}$ as in Figure 4.2, which depicts the beam pattern after reflection from the first OAPM, with the beams aiming into the page. At this spot, there is a mask that blocks all higher diffraction orders. A second delay is implemented using stacked retroreflectors. That is, the bottom two beams are delayed relative to the top two using a second delay line. This length OAPM mirror. In comparison, a 500 nm visible beam would focus to a spot six times smaller, with 36 times the intensity, and potentially $36^3 = 4.7 \times 10^4$ more nonlinear signal intensity.
second delay line creates the delay between the two pumps, i.e. the $\tau$ delay. Referring to Figure 3.1, if the first delay line produces a delay $t_{13}$ between the $k_1$ and $k_3$ beams, we see that $T$ (the delay between the second and third excitation pulses) is simply $t_{13} - \tau$ whenever $k_1$ precedes $k_2$ (corresponding to positive values of $\tau$). Changing the delay $\tau$ will then change the delay $T$ as well. This means that both delay stages must be moved with equal steps in order to keep $T$ constant. On the other hand, if $k_2$ precedes $k_1$ (negative $\tau$) then the second and third pulses are now $k_1$ and $k_3$, and $T = t_{13}$. To summarize this in equation form, we have

$$\tau > 0 \rightarrow T = t_{13} - \tau, \quad (4.1)$$

and

$$\tau < 0 \rightarrow T = t_{13}. \quad (4.2)$$

Equivalently, this information can be depicted diagrammatically, as in Figure 4.3.

Thus, arbitrary time delays can be produced between $k_1$, $k_2$, and $k_3$.

Earlier ultrafast DO-based experiments, such as such the fifth-order Raman experiments on CS$_2$ performed by Astinov et al. [87], employed coincident pulse pairs. Delay stages to control the timing between the pulse pairs were placed before the DO in the beam line. For photon echo experiments, it is necessary to have adjustable time delays between all excitation pulses. In the present setup, the phases of the $(k_1, k_2)$ beam pair are correlated because they are produced from the same beam following the beamsplitter. However,
Figure 4.3: Pulse sequences for positive and negative $\tau$. The time delays $\tau$ and $T$, corresponding to the coherence time and population times in echo spectroscopy, are shown with respect to the delays $t_{13}$ and $T$ set by the two motorized delay lines in the DO setup.

The phases between the pairs are not fixed. But because the echo signal is given by $k_{\text{echo}} = k_2 - k_1 + k_3$, the heterodyne detected phase of the measured photon echo signal is

$$\phi_{\text{het}} = (\phi_2 - \phi_1) + (\phi_3 - \phi_{\text{ref}}) + \phi_{\text{sample}}.$$  \hspace{1cm} (4.3)

So, phase variations between the beam pairs will cancel. The variations in the sample-induced phase, $\phi_{\text{sample}}$, are negligible provided the sample surfaces remain stable so that the fluctuations in the optical pathlengths of the beams remain small.

As discussed in the previous section, the phases of the excitation pulses are preserved provided that they all strike the same optics following the DO. This is true for our setup with the exception of the second retroreflector used to create the $\tau$ delay. The phases of the $(k_1, k_2)$ pair are correlated since they are produced from the same beam, but after the diffractive optic $k_1$ strikes the "fixed" retroreflector, whereas $k_2$ strikes the movable retroreflector on the delay line. Respectively, the same is true for $k_3$ and $k_{\text{ref}}$. Since they do not strike the same optics, this would appear to destroy the phase correlations between $(k_1, k_2)$, and between $(k_3, k_{\text{ref}})$. However, beams $(k_1, k_3)$ strike the
same (top) retroreflector, and beams \((k_2, k_{\text{ref}})\) strike the same (bottom) retroreflector. So for instance, any phase change induced by vibrations and motions of the bottom retroreflector will affect beams \(k_2\) and \(k_{\text{ref}}\) in the same way, and any loss in phase correlation between \((k_1, k_2)\) will be equivalent to the loss in phase correlation between \((k_3, k_{\text{ref}})\). Furthermore, since the heterodyne detected phase depends on the difference between \((\phi_2 - \phi_1)\) and \((\phi_{\text{ref}} - \phi_3)\), any phase fluctuations induced in the retroreflector stages will tend to cancel.

This solution was first realized in the visible photon echo setup by Ogilvie et al. [91], upon which the present setup was based. In this previous work, two solutions for implementing the \(\tau\) delay were realized [80]. One method involved putting glass slides in the beams and rotating them in order to vary the delay. The glass slides are extremely light and can be moved with excellent precision and stability. Over the course of one hour, \(\lambda/90\) phase stability in the visible was achieved using this method. Unfortunately, this scheme provides a limited delay range because slide thicknesses of more than a few mm are impractical in large part due to the induced material dispersion. In addition, the difficulty in finding glasses with broad spectral transparency in the IR render this method less than ideal for the present experiments. The second solution, using stacked retroreflectors as described above, provides phase stability that is about a factor of two smaller. This is because the phase stability depends sensitively on the mechanical stability of the delay stage, which favours the smaller and lighter glass slide setup. However, because of the longer wavelengths, IR spectroscopy inherently provides greater phase stability than visible spectroscopy. \(\lambda/40\) stability was reported using the stacked retroreflectors with 540 nm pulses, but with our IR setup we measured better than \(\lambda/150\) stability over one hour with 3.0 \(\mu\)m pulses.

Experiments and pulse characterizations performed using this new IR diffractive optics setup will now be described. It is important to note that in future work, DO's should prove invaluable in two-colour phase locked experiments. Without a DO, such
experiments would require the locking of the phases between pulses of each colour (likely entailing the active phase locking one OPA relative to another), as well as phase-locking after the pulse pattern is generated using beam splitters. A DO would accomplish both of these tasks by itself, in that it would produce phase correlations between the pulse pairs generated with each colour.

4.3 Pulse characterization - Frequency Resolved Optical Gating in the infrared

Proper pulse characterization is an essential component of any ultrafast experiment. The most basic and common method is autocorrelation. Via a second-order nonlinear process, an intensity envelope of the pulse with respect to time is generated. For an unchirped pulse without any phase distortions, this information together with the spectrum of the pulse would be enough for a full characterization. However, achieving zero chirp and zero phase distortions is an ideal that is seldom realized in practice. Nonetheless, the need to control and measure the amplitude and phase of a pulse is crucial in many fields of ultrafast laser spectroscopy. For instance, regarding the present work, the amount of chirp on a pulse can drastically affect the shape of a 2D-IR spectrum, a fact that will be addressed in greater detail in Section 4.4.

It is well-known that a second-order autocorrelation does not reveal any information about the chirp of the pulse, for the measured signal is a function of intensity only. This method is also time invariant, meaning it is also not possible to distinguish the leading edge of the pulse from the trailing edge. Third-order autocorrelation [92] can determine the direction of time and is more sensitive to wings in the time envelope of the pulse, but it is incapable of measuring the chirp. In principle, it is possible to determine the pulse amplitude and phase from the pulse spectrum and interferometric autocorrelation [93], but the time direction cannot be determined because the second-order nonlinear effects
upon which those measurements rely cannot distinguish the time direction. Also, the numerical procedure for extracting the pulse shape can be extremely complex, requiring a great deal of time to converge to a unique solution.

In the infrared, further problems develop with detector simplicity and availability. Room temperature silicon and InGaAs detectors can be used in the visible and near IR up to only 1.3 \( \mu \text{m} \). Direct detection of mid-IR beams requires the use of thermoelectric or liquid nitrogen (LN\(_2\)) cooled detectors such as PbS, PbSe, InSb, and HgCdTe. Alignment of invisible IR beams into detectors and nonlinear crystals is not a trivial task. Any frequency conversion method involving wavelengths past the near-IR becomes especially troublesome to align when one cannot see the beams. Also, the detectors needed for the fundamental and frequency-converted IR light are often different. For this reason, autocorrelation measurements based on multiphoton absorption in Si or InGaAs are popular in the IR because there is one fewer alignment step compared with methods like SHG autocorrelation [94, 95]. Despite this simplification, a full pulse characterization still requires two measurements, including a third-order correlation, and in general the use of more than one detector will be required. Furthermore, the detectors needed for the experiment and those needed for pulse characterization may be different, and if so, even more frequent swapping and realignment of detectors will be necessary.

The development of Frequency Resolved Optical Gating (FROG) by Trebino in 1993 [96] allowed for unique determination of the amplitude, chirp, and spectral phase of a pulse for the first time. They described one method called SHG-FROG. In this scheme, the pulse is first divided into two using a beamsplitter. One of the beams is then delayed in time relative to the other, and the two pulses are overlapped in a short nonlinear crystal. The chirp is measured by detecting the spectrally-resolved intensity of this SHG-converted output pulse with respect to the delay between the two input pulses. One can then extract the phase by using a FROG algorithm that employs a fit based on the measured chirp and the linear spectrum of the pulse.
An alternative to FROG is a method called SPIDER, which was first proposed by Iaconis and Walmsley [97]. SPIDER requires three replicas of the pulse being characterized — two replicas of the original pulse separated by a scanned time delay $\tau$, and a third, highly stretched pulse. The two replica pulses are then upconverted in a nonlinear crystal, with each one mixing with a different spectral portion of the stretched pulse. The two frequency-sheared upconverted pulses are then interfered in a monochrometer, and spectral interferograms are taken for scanned values of the delay $\tau$. The spectrum and phase can be extracted from these sets of interferograms. One advantage of SPIDER compared to FROG is that pulse dispersion in the nonlinear medium is less significant with SPIDER, because the stretched pulse used for upconversion is already highly stretched in time [98, 99]. This makes for easier characterization of very short pulses. With FROG, the dispersion can be minimized by using a very short medium, but this is done at the expense of the magnitude of the measured signal.

Although the FROG method soon blossomed into several different schemes such as polarization gating (PG), self diffraction (SD) and transient grating (TG) FROG, SHG FROG remains the most commonly used variant. PG FROG is limited by the need for very high contrast, low-loss, broadband polarizers, which is not the case for the other methods. TG FROG is less sensitive than SHG FROG, but does not involve a frequency conversion step. But unlike SD and SHG FROG, TG FROG signals are intrinsically phase-matched at all wavelengths and the signal can be produced over a longer interaction length [100]. This helps offset the difference in sensitivity between the second-order and third order susceptibility in the material. Also, the TG signal is emitted in the distinct direction $k_2 - k_1 + k_3$, making it free of background signals and scattering from the input beams. For many experimentalists, the major drawback of TG FROG is that the input beam must be split into three beams instead of two. The creation and precise alignment of three beams is usually considered to be an impediment for implementing TG FROG as opposed to other methods involving only two beams. However, our TG FROG setup
is identical to our three-pulse heterodyned photon echo setup and requires no additional alignment. As shown in Figure 4.2, photon echo and TG signals are emitted in the phase matched $k_2 - k_1 + k_3$ direction and collimated using an off-axis parabolic mirror with a 10 cm effective focal length. The signal is then focused into a monochrometer and the spectrally dispersed signal is detected on an LN$_2$-cooled 16-element MCT array. To switch between performing a pulse characterization measurement and a photon echo experiment, the only alteration is the replacement of the sample. There is no need to re-align any of the input beams or to switch and realign detectors. It is extremely beneficial in IR experiments to be able to switch between echo and FROG measurements so easily, because the difficult and time consuming task of aligning the invisible beams is eliminated. It is important, though, to check that new samples are placed in the correct focal plane where the beams are overlapped. This is easily done by checking the magnitude of the TG signal emitted at $T = 0$ fs on an integrated detector, and finding the sample position where it is maximized. This ensures that the FROG sample is placed in the focal plane, which can be set by translating the sample using a micrometer stage.

Any material that gives a nonresonant signal in the desired spectral region can be used for TG FROG measurements [100]. We used both CaF$_2$ and c-cut (non-depolarizing) sapphire wafers, with 0.5 or 1 mm thicknesses. Such thin wafers were necessary to minimize the material dispersion in the TG medium. Nonetheless, the observed homodyne TG signal was easily detectable, even when spectrally dispersed. The frequency resolution of the array-monochrometer combination was $\sim 10 \text{ cm}^{-1}/\text{pixel}$ and the monochrometer gratings were used to step the array thirteen pixels at a time in order to capture the entire spectrum. For a sub-100 fs pulse, the time needed to obtain a FROG scan is typically less than 10 minutes.

A sample FROG trace is shown in Figure 4.4. The time delay $T$ was scanned from (-150, 150) fs using 5 fs time steps. Over a range of $\nu_3$ from 3250 to 3650 cm$^{-1}$, the contour gradients run parallel to the $T = 0$ axis indicating minimal spectral chirp. There
Figure 4.4: Sample FROG trace of a mid-IR pulse. The contour gradients run parallel to the $T = 0$ axis (black line) over most of the spectral width of the pulse, indicating minimal spectral chirp.

is some slight chirping on the red edge of the pulse that could not be corrected. For the FROG trace of Figure 4.4, the spectrum and spectral phase was extracted using readily available FROG software (Femtosoft Technologies), the results of which appear in Figure 4.5. Most of the spectrum of the IR pulse is accurately reconstructed by the FROG program, along with a flat spectral phase. The temporal FWHM width of the pulse is 64 fs, giving a time-bandwidth product of 0.47 and indicating that it is very nearly transform-limited.

The pulses acquire significant positive chirp due to the germanium filters placed in the beam paths. There is about 4 mm of germanium in the path of each beam, as a result of the high pass filter that blocks the OPA signal and idler beams; and the attenuation filter (for the reference) and compensating plate (for the three excitation beams). Negatively dispersive optical elements such as CaF$_2$ can be used for compensating positive material
Figure 4.5: IR spectrum and spectral phase extracted by FROG routine. Black curve: experimentally measured linear IR spectrum. Red curve: IR spectrum extracted from the FROG trace of Figure 4.4. Dashed blue curve: extracted spectral phase.

dispersion [101]. The linear group delay in the uncompensated pulses amounts to 0.5—0.6 fs/nm, which was compensated using uncoated CaF$_2$ plates totalling 10 - 12 mm in thickness, resulting in minimally chirped pulses such as that shown in Figure 4.4.

Therefore, it has been shown that full characterization of laser pulses using Transient Grating FROG can be accomplished using the IR DO experimental setup. Absolutely no optics need to be realigned when switching between pulse characterization measurements and nonlinear optics experiments such as photon echo or transient grating spectroscopy. Since TG-FROG requires nonresonant sample materials, there is no upconversion step necessary in order to characterize the pulse and the same detector can be used for both FROG and nonlinear spectroscopy measurements. When alternating between pulse characterization and experiment, all that is required is a change of the sample material. In order to compensate for pulse chirp, CaF$_2$ windows have been used to eliminate first
order chirp in mid-IR pulses as short as 60 fs.

4.4 Further considerations: chirped pulses and non-resonant window signals in the 2D-spectra

In any nonlinear experiment, dealing with nonlinear background signals from sample cell walls is critical. Using homodyne detection, we have observed that the signal from a 0.3 OD sample of H₂O held between two 0.5 mm thick CaF₂ windows is comparable to the signal from the windows themselves. Thus, it is important to characterize the signal produced by the CaF₂ window in order to distinguish its nonresonant signal from the resonant echo signal produced in the water sample.

When the sample is a non-resonant material such as CaF₂, frequency-resolved echo (involving a scan along the τ delay) is nearly equivalent to frequency resolved transient
Figure 4.7: FROG traces corresponding to the 2D spectra in Figure 4.6. Right panel: chirp-compensated pulse using 10 mm of CaF$_2$. Left panel: chirped pulse (no chirp compensation).

Grating (involving a scan along the $T$ delay), provided all three pulses are indistinguishable. The only difference between the two is a time inversion along the scanned time variable. Of course, the latter measurement is the TG FROG measurement discussed in Section 4.3. Thus, a positively chirped pulse in a TG FROG scan will appear negatively chirped when the $\tau$ delay is scanned. When performing the Fourier transform in order to produce the 2D spectrum, this smearing of the signal along $\tau$ will result in a narrowing of the peaks in the 2D spectrum. This effect is evident in Figure 4.6, in which the 2D spectra taken on a 500 $\mu$m thick CaF$_2$ window are compared for chirped and unchirped pulses. The corresponding FROG traces appear in Figure 4.7. For the unchirped pulse, 10 mm of CaF$_2$ was inserted in the beam path for chirp compensation. For the chirped pulse, no compensating material was used. Comparing the 2D spectra using the two types of pulses, the peak in the 2D spectrum using the chirped pulse is about one-third
narrower along $\nu_1$ and more tapered in its overall shape. Thus, chirped pulses can distort features in the 2D spectrum quite noticeably. This illustrates the importance of having well-characterized pulses and minimizing the pulse chirp.

4.5 2D-IR echo of acetic acid dimer

Cyclic acetic acid dimer (CH$_3$COOH)$_2$ represents an important model system for studying basic vibrational couplings such as hydrogen bonding [102, 103, 104, 105]. The linear OH-stretching band is broad and contains many complex features, as depicted at the top of Figure 4.8. Fermi resonance coupling and low frequency modes in the dimer lead to a highly structured inhomogeneously broadened spectrum. The physical origin behind these complicated features involves understanding the various coupling mechanisms present in the dimer.

In this respect, much has been learned from recent ultrafast IR studies of acetic acid. Pump-probe and transient grating measurements have revealed nonexponential decays as well as oscillations in the signals that are consistent with coupling of the OH to intermolecular low-frequency modes [104, 105, 106]. Rapid homogeneous dephasing times of $T_2 = 200$ fs have been observed, which is consistent with spectral hole burning data and provides further evidence for a strongly anharmonic OH-stretching mode [107]. In addition, measurements on the $T_1$ lifetime of the OH stretching and bending modes display very fast relaxation dynamics (200 fs and 250 fs respectively) [108]. The data suggests significant mutual coupling between the bending and stretching modes. In addition, the bending and stretching modes appear to be directly coupled to the low frequency modes, as indicated by the populating of these low frequency modes during the directly observed vibrational relaxation of the OH bend and stretch in the dimer.

These experiments have revealed information on both the multilevel structure and vibrational couplings of the OH stretch. In order to further disentangle the complex
OH stretching spectrum and directly observe the couplings within the acetic acid dimer, femtosecond 2D-IR measurements were performed. The results have been discussed in considerable detail elsewhere [109, 110]. Even though this thesis does not focus on the spectroscopy of the acetic acid dimer, the results are extremely interesting and the 2D spectra that were obtained nicely demonstrate the power of the 2D-IR method, as well as the elegance of the IR diffractive optic technique. Although this author was involved in this work, ultrafast spectroscopy of the acetic acid dimer is a central Ph.D. topic of Nils Huse and for this reason, the results will only be briefly outlined here.

The experiments were performed using pure acetic acid (CH$_3$COOH) dissolved in CCl$_4$ with a concentration of 0.2 M. The solution flowed through a 200 $\mu$m thick sample cell with 1 mm thick CaF$_2$ windows. The OD of the sample was 0.3. The 1 $\mu$J excitation pulses (at a 1 kHz repetition rate) were centred at 2940 cm$^{-1}$ and were 85 fs in duration. The polarizations of all pulses were mutually parallel. The coherence time $\tau$ was scanned at constant population time $T$, and the echo signal was heterodyne detected using spectral interferometry. The spectral fringes were measured using a 16-element LN$_2$-cooled HgCdTe array.

The 2D-IR spectra for $T = 0$ fs and $T = 400$ fs appear in Figure 4.8. The plots display the amplitude of the heterodyne-detected echo signal as a function of the excitation frequency $\nu_1$ and the detection frequency $\nu_3$. The linear IR spectrum also appears for comparison purposes. The most prominent features are the peaks along the diagonal at $\nu_1 = \nu_3 = 2920$ cm$^{-1}$ and $\nu_1 = \nu_3 = 2990$ cm$^{-1}$, corresponding to analogous features in the linear spectrum. These appear due to ground state bleaching of the $\nu = 0$ state followed by stimulated emission from the $\nu = 1$ state. The corresponding cross peaks are also clearly visible. As discussed in Chapter 3, these cross peaks occur due to coupling between the transitions. When the excitation at a particular transition couples to another transition there is a transfer of amplitude to a different (detected) frequency. In the $T = 0$ plot, there is another off-diagonal peak that is red-shifted off of the diagonal along...
Figure 4.8: (a) Linear spectrum of the O-H stretching band of cyclic dimers of acetic acid in CCl₄ (solid line). Also shown are cross sections through the 2D vibrational spectra at an excitation frequency of 2920 cm⁻¹ for population times $T = 0$ (dashed line) and 400 fs (dash-dotted line). (b,c) Two-dimensional vibrational spectra of cyclic acetic acid dimers (inset in (c)) measured for population times of $T = 0$ and 400 fs. The absorptive component of the photon echo signal is plotted as a function of the excitation frequency $\nu_1$ and the detection frequency $\nu_3$. 

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the direction of detection axis. This is the induced absorption from the \( \nu = 1 \) to \( \nu = 2 \) vibrational level. These types of features are analogous to those pictured in the schematic diagram of Figure 3.2.

It is clear that features along axes at constant values of \( \nu_3 \) in the 2D spectrum are well-aligned with features in the linear IR spectrum, such as the peaks near \( \nu_3 = 2625 \text{ cm}^{-1} \), \( 2685 \text{ cm}^{-1} \), and \( 3100 \text{ cm}^{-1} \). As expected from the 2D-IR method, the nonlinear response has been stretched across the detection frequency axis.

By \( T = 400 \text{ fs} \), the \( \nu = 1 \rightarrow \nu = 2 \) excited state peak has vanished, which is consistent with the experimentally observed 200 fs population time \( [108] \). The ground state bleach persists because the \( \nu = 1 \) state has been shown to decay via intermediate states that are different from the \( \nu = 0 \) ground state. The ground state only becomes repopulated after tens of picoseconds \( [108] \). These conclusions from the earlier literature are further confirmed by the spectral slices through 2920 cm\(^{-1} \) that appear in Figure 4.8. Between \( T = 0 \) and 400 fs, the excited state absorption decays away, along with some spectral decays across the detection frequency axis.

Calculations of the linear OH stretching band and the nonlinear 2D spectra were performed using density functional theory. Since the excited state contribution has decayed by \( T = 400 \text{ fs} \), this experimental plot was compared with preliminary theoretical results that were calculated using only \( \nu = 0 \leftrightarrow \nu = 1 \) quantum pathways. By comparison with theory, pronounced Fermi coupling is found to be responsible for the most prominent features in the experimental 2D spectrum. For instance, the peak at 2921 cm\(^{-1} \) is mainly due to a \( \nu_{a_0} \text{C-O} / \nu_{a_g} \text{C}=\text{O} \) combination band that is coupled to the O-H stretch via a Fermi resonance, which is due to an approximate degeneracy between the two vibrational transitions. More details on the calculated spectral features and coupling constants can be found in the associated paper by Huse \emph{et al.} \( [110] \).

The anharmonic couplings to low frequency modes that were observed in previous work \( [107] \) are difficult to discern within the 2D spectra. By plotting the spectrally
resolved echo frequency $\nu_3$ vs $\tau$ (i.e. without Fourier transforming the $\tau$ coordinate), it becomes clear that these recurrences are indeed contained within the data [109].

In summary, 2D-IR spectroscopy on acetic acid dimer has been performed using the new diffractive optic-based setup. The features in the 2D spectra and the O-H absorption band are dominated by Fermi resonances with combination bands of C-O, C=O, and other fingerprint vibrations. The cubic coupling constants $\phi$ are in the 40-150 cm$^{-1}$ range. The wealth of information obtainable using 2D-IR spectroscopy is evident in these studies and helps establish the methods needed for dissecting the dynamics involved in the hydrogen bond network of H$_2$O.
Chapter 5

The structure of water: what is already known?

5.1 Introduction and separation of structural time scales

Water is the most common liquid found on our planet. Chemical reactions that take place in aqueous environments form the basis for life. It is therefore no great surprise that water has been the subject of such intense scientific research.

The molecule itself is a simple triatomic. Nonetheless, understanding the structure and dynamics of water is an extremely challenging scientific problem. The water molecule is symmetric and consists of two light hydrogen atoms and a heavy oxygen atom with the angle formed by the H-O-H bonds falling in the $104.5^\circ - 106^\circ$ range. The bond angles and bond lengths were first determined using rotational and vibrational water vapour spectra data as observed by Benedict et al. [9]. In the liquid form, its five-molecule hydrogen bonded structure can be depicted by the schematic diagram of Figure 5.1. Each water molecule’s ability to form up to four hydrogen bonds makes water wholly unique amongst all other hydrogen bonded compounds. The presence of tetrahedral structures as shown

in the figure has been known since the first X-ray diffraction experiments in water by Morgan and Warren [11]. However, the configuration in Figure 5.1 is not unique, in that configurations involving rotated orientations of the outer molecules or variations of the lengths of the O-H bond and/or the O-H-O hydrogen bond are also possible.

Water has several anomalous properties that differentiate it from other liquids. Many of these properties have been conveniently catalogued in reviews by Chaplin [111] and the classic text by Eisenberg and Kauzmann [2]. For instance, compared to other Group VI Hydrides (i.e. $\text{H}_2\text{S}$, $\text{H}_2\text{Se}$, $\text{H}_2\text{Te}$), water has an unexpectedly high melting point and high boiling point. Also, anyone who has ever filled an ice tray surely knows about the density anomaly of water, namely, that water expands upon freezing as its density decreases. When heated above $0^\circ\text{C}$, the density of water increases, reaching a maximum at $\sim 4^\circ\text{C}$. But for most liquids, the density increases upon freezing, and decreases when heated over any temperature range. Clearly, a successful microscopic description of water should account for these unusual properties.
Chapter 5. The structure of water: what is already known?

Explanations for these anomalies almost always relate back to hydrogen bonding in water. Although hydrogen bond forces are not unique to water, it has the highest fraction of hydrogen bonds of any substance. Understanding this hydrogen bond network is crucial in order to understand the physics and chemistry of this liquid. Consider, for instance, the heat capacity, \( C_v \) in the solid, liquid and gas phases. The temperature dependence of \( C_v \) in steam is due to the changes in potential and kinetic energy of the individual vibrating and rotating molecules. Similarly, \( C_v \) in ice increases slightly as it is heated. Since the crystal structure in ice is independent of temperature, the increase in \( C_v \) is due to the excitation of intermolecular vibrations. Surprisingly, \( C_v \) for (liquid) water is a factor of two larger than ice or steam. The vibrational contribution, which is nearly the same as it is in ice, can only account for about half of the observed \( C_v \). The increased heat capacity is due to a configurational contribution that depends on changes in the local substructure of the liquid as it is heated. Breaking or deforming of hydrogen bonds results in a contribution to \( C_v \) that is nearly as large as that from vibrations throughout the liquid phase.

This thesis investigates the dynamical properties of water molecules and the surrounding hydrogen bond network. In order to quantify these concepts further, it is necessary to clarify the time scales of various vibrational motions in the liquid. The answer to a question such as "what is the structure of the liquid?" depends completely on the time scales on which it is observed.

As a starting point, consider the structure of ice, in which the molecules are held in a fixed, rigid formation on ultrafast time scales. In this context, "rigid" means that the centres of mass of the individual molecules in the crystal lattice essentially do not move relative to the timescales of their diffusional and rotational motions. This is the stationary, or static structure of the crystal – in which the mean positions of the molecules are determined once all the motions around their equilibrium points have averaged out. This is known as the D-structure (diffusion averaged structure) of ice [2].
In this regard, IR and Raman spectroscopy have been used extensively to determine the vibrational structure of liquid H$_2$O and D$_2$O [112]. These experiments produce what are known as static spectra and provide insight into the D-structure. The Raman spectrum of liquid H$_2$O appears in Figure 5.2. The most prominent feature is the broad (~250 cm$^{-1}$ wide) peak centred near 3400 cm$^{-1}$, which represents the OH stretching vibration. Since hydrogen bonds in water occur between the hydrogen atom in an OH bond and an oxygen atom on a nearby molecule, i.e. an OH...O bond, the OH is directly coupled to the hydrogen bond network that is responsible for so many of the unique properties of the liquid. Therefore, much effort has gone into examining the OH stretch vibration in order to obtain information about water structure. Evidence of a multi-component structure of water, possibly involving hydrogen bonded and non-hydrogen bonded molecules, has been inferred through Gaussian deconvolution of its IR and Raman spectra. Since Raman spectra are diffusion-averaged measurements, those assignments do not provide direct insight into the dynamics of water on the timescales of the vibrational motions. With these goals in mind, femtosecond IR spectroscopy has been extensively employed over the last decade, albeit mainly using isotopic HOD:D$_2$O as a substitute for pure water. These experiments will be described in further detail in the next section.

The peak near 1650 cm$^{-1}$ is due to the H-O-H bending motion. The bend overtone occurs near 3250 cm$^{-1}$, partially overlapped with the OH-stretch. This can lead to coupling to the OH-stretch vibration via Fermi resonances, thereby affecting the shape of the IR and Raman OH spectra. The broad peak stretching from 300 - 1000 cm$^{-1}$ represents the librations, or hindered rotations of the H$_2$O molecule. At even lower frequencies, below 200 cm$^{-1}$, are features corresponding to the hindered translational modes. These appear within a shoulder rising from the low frequency end of the libration band. In that shoulder, the Raman spectra display two prominent peaks, one near 170 cm$^{-1}$, and the second near 60 cm$^{-1}$. The first corresponds to the stretching motion of the H-bond along the O-O separation, and the second to the hindered translations associated
Figure 5.2: Raman spectrum of liquid water, reprinted with permission from reference [112], copyright 1964, American Institute of Physics. The most prominent feature is the broad peak centred near 3400 cm\(^{-1}\), which is attributed to the OH stretch vibration in the liquid.

with H-bond motions, in other words, the shearing-type motions of the water pentamer clusters.

On time scales faster than the diffusional kinetics, molecules can undergo re-orientations, or rotations, due to thermal motions. Considering ice once again, this happens on time scales of \(\sim 10 \mu s\). So on time scales shorter than this but slower than the vibrational periods of the individual molecules, one would observe the vibrationally averaged structure, or V-structure [2]. A hypothetical camera with an exposure time within the range of 10 \(\mu s\) - 1 ps would freeze the rotations of the molecules, making their relative orientations appear random, rather than part of a ordered lattice structure. However, the motions of atoms within the molecule itself would not be frozen since the motions of the OH stretch and bend are much faster and would be averaged on 10 \(\mu s\) - 1 ps time scales. The same would be true of the sub-picosecond librational motions. It follows that since the rotational motions occur on the same time scale that H-bonds are formed and broken, the average molecular positions in the lattice will not appreciably change on these time scales. Thus, any one molecule will look the same as it does on diffusion-averaged time
scales, but the arrangements of the molecules that surround it will appear more random. Since the H-bond vibrational frequency is 170 cm\(^{-1}\) (equivalent to a 200 fs vibrational period), modulations in the H-bond network will occur on a time scale faster than that of the V-structure. The geometry of the network, corresponding to which H-bonds are present and how the molecules are arranged relative to each other, will not change on the 1 ps - 10 \(\mu\)s time scales of the V-structure.

On sub-ps time scales, we must consider the atomic motions within the molecules. The translation and libration modes have been already mentioned, but on even faster time scales (below 200 fs), the oscillations (in ice) of the O-H bend at 1650 cm\(^{-1}\) and the O-H stretch at 3220 cm\(^{-1}\) are no longer averaged either. In a photo taken by a hypothetical camera with an exposure time < 10fs, the atomic positions will no longer appear “blurred” since the motions of the individual atoms will not be averaged out, and no atomic equilibrium positions will be clearly evident. On these fastest time scales, we are observing the instantaneous, or I-structure, since we are (in principle) able to capture the actual bond oscillations and resolve the positions of individual atoms within molecules.

In the liquid phase, the picture is slightly more complicated because the clear divisions between the time scales begin to disappear. Of course, water molecules do not retain an ordered crystal structure like ice molecules do. In the liquid, molecules move more freely due to thermal diffusive motion. The V and D-structures in liquid water are about the same order of magnitude, with fluctuations in both occurring on picosecond time scales. Thus, dissection of the V-structure in liquid water becomes difficult because of the very short time resolution that is required in order to study it. At present, nonlinear spectroscopies using ultrafast lasers are the only types of experiments that are sufficient for making time-resolved measurements on these sub-picosecond timescales.
5.2 X-ray diffraction of water

X-ray diffraction studies have revealed a great deal of information about the static, D-structure of water. Unlike the IR and Raman spectroscopies, X-ray diffraction experiments can directly measure spatial structures and distance correlations between molecules. What is experimentally measured is an X-ray diffraction intensity $I(s)$, where $s$ is the amplitude of the scattering vector and is related to the scattering angle $2\theta$ by the relation $s = 4\pi/\lambda \sin \theta$. The diffraction intensity is given by [2, 113]

$$I(s) = \langle F^2 \rangle + \langle F^2 \rangle \int_0^\infty 4\pi r^2 \rho_0 dr g(r) \frac{\sin(sr)}{sr}.$$  \hspace{1cm} (5.1)

In this expression, $\langle F^2 \rangle$ is the total scattering intensity from the molecule at the origin (cf. the central molecule in the five-molecule structure of Figure 5.1). The expression also assumes spherical symmetry in that $I(s)$ depends only on the magnitude of molecular displacements $r$ and not on the orientations of the molecules. Also, $\rho_0$ is the average density of the liquid, and $g(r)$ is the radial distribution function. $g(r)$ is the key piece of information pertaining to the local density of molecules, and it can be defined as

$$g(r) = \frac{\rho(r)}{\rho_0},$$  \hspace{1cm} (5.2)

where $\rho(r)$ is the average density of water molecules within a sphere of radius $r + dr$ around any molecule. It is time independent and represents the time-averaged local density of molecules at a distance $r$ from any central molecule — in other words, the D-structure of the liquid, as stated in Section 5.1. For large $r$, $g(r) = 1$ because the liquid will necessarily resemble the bulk over very large volumes. However, when $r$ is of the order of intermolecular distances, $g(r)$ will vary from unity because the forces between molecules will affect their relative positions. Peaks are expected at values of $r$ where molecules are most likely to be found, with the widths of the peaks representing the uncertainty of their positions.

The X-ray diffraction results by Narten and Levy [113] for water appear in Figure 5.3.
Chapter 5. The structure of water: what is already known?

Figure 5.3: The O-O distance correlation function of H$_2$O, measured using X-ray diffraction spectroscopy. The figure is reprinted with permission from reference [113], copyright 1971, American Institute of Physics. At 4°C, the average nearest neighbour O-O correlation distance is 2.8 Å. As water is heated, this correlation distance becomes larger, and the distribution of O-O distances (i.e. the width of the correlation peak) also becomes larger. Also at elevated temperatures, the second and third correlation peaks no longer appear. Both these observations reflect the weakening of the hydrogen bond network and the greater disorder [114] in the liquid.

The X-ray scattering centres in water are near the oxygen atom and therefore $g(r)$ represents the correlation function for O-O distances. Near 4°C, a sharp peak corresponding to the first coordination shell of water appears at $r = 2.8$ Å. A second peak, corresponding to the second coordination shell, appears near $r = 4.5$ Å, along with a third peak in the range near $r = 6.5 - 7.8$ Å. The central molecule is more weakly affected by the intermolecular forces resulting from the positions of molecules at larger $r$, leading to greater uncertainty in the positions of molecules as $r$ increases. In this sense, the exact positions of the molecules are not known for larger $r$ and the density within such a sphere

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Figure 5.4: X-ray and neutron scattering of H$_2$O data under ambient conditions. The function $g_{oo}(r)$, the correlation function for O-O displacements as a function of $r$, is plotted for the data sets of three different experimental efforts. The figure is reprinted with permission from reference [115], copyright 2002, American Chemical Society. The Thin solid line: X-ray data from Narten and Levy [113]. Dot-dash line: neutron data from Soper et al. [116]. Thick solid line (labelled “ALS”): X-ray data from Hura et al. [117]. Relative to the Narten work, the first correlation peak in the newer X-ray data is sharper and shifted to slightly lower $r$.

of radius $r$ approaches the bulk density $\rho_o$, and $g(r)$ approaches unity, as expected.

More recent X-ray and neutron scattering results were presented and compared in the review by Head-Gordon and Hura [115]. Besides the X-ray data by Narten and Levy, Figure 5.4 shows newer neutron scattering data from Soper et al. [116] and X-ray data from the Advanced Light Source at Lawrence Berkeley National Laboratory by Hura et al. [117]. All three sets of data in the figure were compiled under ambient conditions. Relative to the earlier data from Narten and Soper, the first correlation peak in the newer X-ray data is sharper and shifted to slightly lower $r$. The second and third correlation peaks are in good quantitative agreement. Technological advances in X-ray sources and
CCD detectors are believed to account for the possible inaccuracies in the older data [115]. Qualitatively though, the older X-ray work does capture the essential features in the radial distribution function.

From Figure 5.3, it is clear that as water is heated, the average O-O displacement in the first coordination shell increases. Also, the spread in the distribution of the O-O displacement becomes larger, as evidenced by the broadening of the first coordination peak. As the relative displacements between the molecules increase, their potential energies also increase. This extra potential energy comes from the decrease in the bond strength between the molecules; i.e., hydrogen bonds are broken or weakened, leading to changes in the local configuration of molecules. Using the data from these diffraction experiments, we can propose some details about the hydrogen bond structure, but we can infer nothing about how the H-bond structure is modulated on the time scales of the H-bond vibrations themselves.

### 5.3 What can be learned from ultrafast echo spectroscopy of water?

With respect to theoretical models for water, various basis sets have been used and compared to the data discussed in Section 5.2. It is telling that a wide range of models – polarizable and non-polarizable, rigid and flexible – have all provided very good fits to the radial distribution function $g(r)$ [8]. Although such information is highly useful, the experimental observations obtained by “static” methods such as X-ray spectroscopy are sensitive only to macroscopic properties such as the density and not to the intermolecular forces of interest. It is here that 2D-IR spectroscopy can be of great use in refining theoretical models for liquid H$_2$O. In the preceding sections, the issue of “structure” was addressed with respect to both the time scales of the molecular motions and also the positions of the molecules. In an optical experiment, it is possible to determine
the former but typically not the latter. On the other hand, multi-dimensional nuclear magnetic resonance (NMR) has been used extensively for decades for determining both dynamics and structure [64]. Although extremely successful for determining millisecond dynamics and structure (i.e. D-structure) of molecules, it is not suitable for investigating the V and I-structures. The RF pulses, with frequencies in the tens of MHz range, are not short enough to resolve dynamics on times scales faster than milliseconds. Optical pulses can probe much faster motions; but unlike magnetic spins, vibrational and electronic transitions are not necessarily two-level systems. This means that in general a unique, one-to-one determination of structure from optical echo spectra is not possible.

Nonetheless, with the development of femtosecond, mid-IR sources, dynamics on ultrafast time scales comparable to molecular motions can now be observed. These sources can be tuned to the excitation frequencies of many common vibrational transitions such as the mid-IR fingerprint region near 5 μm. Also accessible (in particular for the purposes of this study) is the region covering the hydroxyl (OH) group in water, which is centred near 3400 cm\(^{-1}\) in the liquid phase. It has long been understood that the OH vibration is coupled to the hydrogen bond network in water [1]. Neighbouring molecules couple to each other via an intermolecular OH\(..O\) bond and excitation of this OH group should provide a direct window on the workings of the H-bond network.

It has also long been understood that the OH stretch in liquid water is anomalously broad [10]. Gas phase IR spectra of water consist of hundreds of narrow features of sub-wavenumber spectral width. In contrast, the liquid IR and Raman spectra contain a single broad OH-stretch feature that is hundreds of wavenumbers in width (Figure 5.2). Why is this the case, and how can we relate the shape and breadth of this peak to the earlier discussion of V and I-averaged structures?

In the language of photon echo spectroscopy, we need to question whether the OH-stretch is highly broadened due to homogeneous or inhomogeneous broadening. Couplings between molecules will result in changes in local substructures. Reconfigurations in the
hydrogen bond network local to a given oscillator will alter the oscillation frequency of that particular vibration. These are homogeneous broadening mechanisms. The I-structure will obviously fluctuate with time, but in a homogeneously broadened sample, the V-structure will also fluctuate with time.

On the other hand, inhomogeneous broadening occurs due to static local environments. In this case, “static” means that if a system is fully inhomogeneously broadened over a particular time scale, then the V-structure will not fluctuate on that time scale. Rather, the broad spectrum is the result of a wide variety of existing local substructures, which suggests that the H-bond network does not change with time and that there no dynamic coupling between oscillators exists. We know from the X-ray diffraction data that local ordering does in fact exist in the liquid, thereby presenting some indirect proof of the local substructure in the vicinity of a given molecule. However, we cannot say for certain that water is partly inhomogeneously broadened unless we know the time scales for which this ordering persists. The time scale over which this inhomogeneity exists was an unsolved problem and it is exactly this problem that has been solved in this thesis work.

5.4 Previous studies of water and isotopically substituted water using ultrafast spectroscopy

Studying pure liquid water using mid-IR spectroscopy presents a considerable technical challenge. The absorption of the liquid at the centre of the OH stretching band is quite large due to the high (111 M) density of OH oscillators in water [118]. The 1/e absorption length at 3400 cm\(^{-1}\) is only 400 nm. Equivalently, the optical density (OD) of a 400 nm thick sample of pure H\(_2\)O is about 0.43. Optical signals also experience significant distortions when propagating through samples with OD > 0.3 [119]. These limitations necessitate using samples with extremely short pathlengths only 200 - 300 nm
Chapter 5. The structure of water: what is already known?

thick, even at the expense of substantially smaller nonlinear signals and the need for more sensitive detection methods. The sample preparation methods used in this thesis work are described in Sections 6.1 and 6.2, with particular emphasis on the use of nanofluidic sample cells designed specifically for these ultrafast IR experiments.

For these reasons, most previous femtosecond studies of water have used isotopic water mixtures of HOD diluted in D$_2$O or H$_2$O as a substitute for pure H$_2$O. It was believed that isotopically substituted water systems would faithfully reproduce the key dynamics of a pure H$_2$O system. From the overview in Section 5.6 and the results presented in Chapter 6, it will become apparent that the significance of the fully resonant hydrogen bonded relaxation pathways were not fully appreciated. The most common experiments in this regard have been the studies of the OH stretch in HOD:D$_2$O. Typical concentrations of 0.5% allow for 0.3 OD samples with ~ 100 μm pathlengths, which is a more easily workable sample cell thickness. But it is crucial to note that the vibrational frequency of the OH is very far removed from that of the OD stretch in the surrounding bath molecules (centre frequencies of 3400 cm$^{-1}$ for OH vs 2500 cm$^{-1}$ for OD). The OH stretch is decoupled from its environment since it is not resonant with the OD stretch frequencies in the surrounding bath. The intermolecular couplings between the excited HOD molecules and the D$_2$O bath are expected to be drastically different than in the all-resonant case of pure H$_2$O. Nonetheless, such experiments do provide substantial insight into the localized picture of the OH dynamics.

Picosecond studies in HDO:D$_2$O were first done by Graener et al. in 1991 [120]. Using 11 ps excitation pulses, they inferred a $T_1$ relaxation time of 8 ± 2 ps using transient hole burning spectroscopy. Rey and Hynes used a flexible point-charge model for D$_2$O and performed a Molecular Dynamics simulation to attempt to explain these results [121]. Their model predicted a relaxation time of 7.5 ps. However, they made some crucial assumptions. First, when considering the coupling between the vibrational stretch and bend vibrations, they assumed that rotational relaxation is much faster than vibrational
relaxation. Second, they assumed that the vibrational relaxation rate should be far slower than the period of the OH vibration, an assumption that was partially justified from Graener's results. As a result of these strict separations of the relevant time scales, the coupling between vibrations and all other degrees of freedom was assumed to be small and the coupling Hamiltonian could be analyzed using perturbation theory. Thus, these assumptions lead to a model in which solute vibrational and rotational motions are frozen (i.e. averaged out) and calculations are done with the solute molecules in static equilibrium positions. As we shall see, this is not an accurate picture for HOD:D$_2$O, let alone pure H$_2$O. As for the experimental results of Graener et al., they did not have pulses short enough to resolve the proper time dynamics of HOD:D$_2$O, and the high pulse energies used ($\sim 50 \mu J$) likely led to large temperature increases that can severely lengthen the relaxation dynamics [122].

Subsequently, experiments using femtosecond pulses were carried out by other researchers. With far better time resolution, vastly different time dynamics in HOD:D$_2$O solutions were observed. Using two-colour pump-probe spectroscopy, a multi-component picture of water began to develop. Non-exponential decays of the pump-probe and rotational anisotropy data [123, 124] suggested that the faster decay mechanisms correspond to modulation of H-bond lengths, and the slower decay mechanisms correspond to reorganization of the hydrogen bond network via orientational diffusion.

The roles of the hydrogen bonding and the vibrational relaxation pathways were further quantified by Gale et al. [125], who showed that $T_1$ increased monotonically from the red to the blue regions of the OH stretch. These results were explained by arguing that the red edge of the OH-stretch has greater overlap with the overtone of the OH-bend (centred near 3250 cm$^{-1}$), leading to Fermi resonance coupling in the region where the two bands overlap and a more efficient vibrational relaxation via the pathway through the bend overtone. On the other hand, Bakker et al. [126] claimed a similar frequency dependence of $T_1$, but favoured an interpretation based upon the
strength of the hydrogen bonds coupled to those oscillators. That is, the more strongly hydrogen bonded molecules on the red edge of the OH band relax faster because they couple more strongly to the surrounding bath molecules. Subsequently, both Gale and Bakker's additional interpretation of the H-bond as a strongly overdamped oscillator was superseded by work in which H-bond oscillations have been directly observed in vibrational echo experiments [127, 128]. This will be discussed in the next section. Gale et al. also assumed a straightforward linear relation between the OH·O displacement and the frequency of the OH stretch. More realistically, as proposed in recent theoretical work, there is a complex arrangement of possible molecular orientations for any given OH stretch frequency [129, 130]. In other words, there exists considerable dispersion between the frequency of the OH stretch and the angle that the H-bond makes with the O-O displacement vector. Nevertheless, it is generally agreed that the $T_1$ lifetime for the OH stretch in D$_2$O is around 700 fs, which was measured using two colour pump-probe spectroscopy [131], and rotation-free signals from anisotropy decays [132]. These results showed reasonable agreement with then-contemporary theory [133, 134].

Transient absorption measurements on the OD stretch of HOD:H$_2$O by Steinel et al. yielded quite different results [135]. They observed a longer, frequency-independent $T_1$ of 1.5 ps, as well as a frequency-independent rotational orientation time of 1.5 ps. Together with an H-bond breaking time of $\sim$ 1 ps, this suggests that the HOD molecules are rigidly held in place and cannot reorient until bond breaking occurs. They also observed spectral diffusion on a 500 fs time scale, in particular, showing that 95% of the vibrational linewidth of the OH-stretch is sampled during the first picosecond after excitation. Thus, during the first 500 fs, the rate of vibrational relaxation is frequency dependent but by the time the excitation decays into the ground state it has sampled almost the entire OH linewidth and washed out any frequency dependence of $T_1$. Conversely, the frequency dependence $T_1$ observed by Bakker et al. and Gale et al. is partly due to the lifetime being approximately the same magnitude as the timescale of the spectral diffusion. There
is not enough time for the excitation to sample the entire OH linewidth before the excitation reaches the ground state via vibrational relaxation, and therefore some frequency dependence of $T_1$ remains. These contrasting results indicate that vibrational relaxation of the OD stretch in HOD:H$_2$O is not the same as that of the OH stretch in HOD:D$_2$O.

### 5.5 Photon echo studies of bulk water and isotopic water mixtures

The first photon echo measurements on HOD:D$_2$O were performed by Stenger et al. [136]. The peak shift was found to be dependent on the pump frequency, with larger peak shifts occurring at lower pump frequencies. This is consistent with the vibrational relaxation experiments described previously, because of the stronger H-bonds on the red edge of the OH-band. These stronger bonds lead to faster relaxations but also greater inhomogeneity than the more disordered assortment of molecules associated with the weaker H-bonds on the blue edge. The measured pure dephasing time was 90 fs, approximately midway between the dephasing times they calculated for the cases of a purely homogeneous and purely inhomogeneous liquid. In later experiments, the peak shift and the frequency correlation function of the excited OH stretch were quantified over longer time scales. They observed 700 fs and 5-15 ps components in the frequency correlation function $C(t)$, and both components were ascribed to hydrogen bond rearrangement dynamics. The longer component denotes the presence of a hot, blue-shifted ground state that is due to thermal excitation of the low frequency modes in the liquid [137]. Microscopically speaking, this indicates a 700 fs loss of memory in the persistent hydrogen bond correlations around the excited OH, followed by - on 5 - 15 ps time scales - the molecules settling into a new correlated structure that is random relative to the OH oscillator's initial surroundings.

Subsequent experiments by other groups used shorter, sub-100 fs IR pulses and were able to extract a faster 150-200 fs component in $C(t)$. This has been attributed to
underdamped H-bond oscillations [138] and to H-bond breaking [127]. Multidimensional IR spectroscopy on HOD:H$_2$O, in which the OD stretch is excited within a bath of H$_2$O molecules, has produced qualitatively similar results [128]. In all these isotopic mixtures, $C(t)$ undergoes a fast initial decay and then persists for picoseconds. This indicates that some structure correlation must exist in the liquid on picosecond time scales. Strangely, these more recent experiments have failed to elaborate on the 5-15 ps dynamics associated with the blue-shifted hot ground state. Nevertheless, the overall picture in both HOD:D$_2$O and HOD:H$_2$O is one of underdamped H-bond fluctuations on 100-200 fs time scales as well as H-bond network rearrangement on 1-2 ps time scales.

5.6 Femtosecond spectroscopy of pure H$_2$O

It should have been expected that pure H$_2$O would behave quite differently from these HOD:D$_2$O model systems. When exciting the OH stretch in HOD:D$_2$O, the vibrational frequency of the OH is far removed from the vibrational frequency of the surrounding liquid (a difference of almost 1000 cm$^{-1}$). Such experiments observe the localized OH and hydrogen bond dynamics. In pure H$_2$O, the excited OH group can resonantly couple to adjacent water molecules. Compared to HOD:D$_2$O, the excitation can spatially sample more of the surrounding hydrogen bond network and possibly open up new relaxation pathways with drastically altered dynamics.

Apart from this thesis work, very few femtosecond IR experiments have been done using pure H$_2$O. None of these employed the 2D-IR method in order to dissect a complicated line shape such as the hydrogen bond modulated OH spectrum. Nevertheless, extremely useful information has been obtained using these nominally 1D spectroscopic methods. As expected, the observed dynamics differ quite strongly from those in HOD:D$_2$O. The first such experiment was performed by Woutersen and Bakker [139] and the key results are shown in Figure 5.5. Measurements of the rotational anisotropy in pure H$_2$O were
Figure 5.5: Comparison of the rotational anisotropy decay in HOD:D$_2$O and pure H$_2$O. The figure is reprinted with permission from reference [139], courtesy of Nature Publishing Group and S. Woutersen. For the isotopic mixtures, the decay occurs on picosecond time scales. For pure water, a sub-100 fs decay is observed, suggesting extremely rapid energy transfer and modulation of the hydrogen bond network in the liquid.

performed using 200 fs mid-IR pulses and a water sample that was one micron thick. These samples were produced by squeezing water between plane CaF$_2$ windows. Even in moderately dilute 17.6 M HOD:D$_2$O (a 6:1 dilution compared to 111 M pure water), the anisotropy decays on a ~ 1 ps time scale, considerably slower than the sub-100 fs decay in pure H$_2$O. This suggested that the vibrational energy transfer between molecules – a process that they believed to be modulated by the hydrogen bond network – takes place in less than 100 fs.

Using an IR-pump and a (visible) anti-Stokes Raman probe technique, Pakoulev et al. [140, 141, 142] expanded on earlier work done by the same group on H$_2$O and HOD:D$_2$O [143]. With pure H$_2$O, they claimed to directly observe relaxation of the OH stretch in pure H$_2$O into the OH bend. They claimed a 550 fs $T_1$ lifetime for the stretch, and the subsequent lifetime of the bend ($\delta_{OH}$) was also measured and claimed
to be 1.4 ps [142]. Around the same time as their work, the $T_1$ lifetime in H$_2$O was measured by Lock and Bakker using pump-probe spectroscopy, and a value of 260 fs was claimed at room temperature [144]. Despite the inconsistencies in the H$_2$O results by the different groups, it is clear that all such results differ strongly from previous results obtained with HOD:D$_2$O. It is absolutely certain that the pure liquid, in which the solute is identical to the solvent and all oscillators in the system are resonant with each other, is a fundamentally different system than the dilute HOD:D$_2$O mixtures where the excited OH is isolated from the surrounding bath molecules.

In summary, many ultrafast studies of water have appeared in the literature in recent years. Some of these were studies of isotopic HOD:D$_2$O mixtures, which is a drastically different physical system than pure water, as evidenced by comparing the results of experiments using H$_2$O and HOD:D$_2$O. Vibrational relaxation is considerably faster in H$_2$O. This observation is just one manifestation of the effect of a spatially extended – resonant – hydrogen bond network on the liquid dynamics. Until this thesis work, the very significant impact this resonant coupling has on the intermolecular dynamics was not appreciated. The dynamics of pure H$_2$O are more than an order of magnitude faster that those in HOD mixtures and there are no longer separations in time scales that enable a well-defined basis to describe the water dynamics. Pure water is fundamentally very different from isotopically substituted water systems. Using the 2D-IR method, information pertaining to the proposed multi-component structure of pure water can be extracted through a photon echo study of the liquid, providing considerable insight into the homogeneous and inhomogeneous broadening mechanisms of water. This thesis represents the first photon echo study of pure H$_2$O, and in turn, constitutes the first direct observation of the fundamental dynamics of water under the fully resonant conditions pertinent to the special properties of this remarkable liquid.
Chapter 6

Two-dimensional infrared spectroscopy of pure liquid H$_2$O

6.1 2D-IR echo of H$_2$O using CaF$_2$ sample cell windows

The extremely high absorptivity of the OH stretch region in water [118, 145] necessitates the use of thin samples that are less than one micron thick. Furthermore, propagation effects in high optical density (OD) samples will distort the shapes of peaks in 2D spectra [119], meaning the ideal sample OD should fall in the 0.2 – 0.3 OD range (~ 200 - 300 nm thicknesses). To meet this requirement, thin samples were prepared by squeezed H$_2$O between two 500 µm thick CaF$_2$ windows. The stainless steel sample cell containing the windows was sealed using Teflon tape, O-rings, and vacuum grease. This combination provided excellent sealing, with the samples retaining a stable, uniform thickness for up to days at a time. In addition, 250 µm sapphire windows were also used in the sample cells. These thinner windows contributed less nonresonant electronic signal. Plus, sapphire’s excellent thermal conductivity led to more efficient heat transport away from the beam focal area and less local heating of the sample.
CHAPTER 6. TWO-DIMENSIONAL INFRARED SPECTROSCOPY OF PURE LIQUID H₂O

The ~ 1 μJ excitation pulses were 70 fs in duration and were centred near 3350 cm⁻¹. In the following data sets, the polarizations of all pulses were mutually parallel, unless stated otherwise. The peak OD’s of the H₂O samples were in the range of 0.25 – 0.30. Scans along τ at constant values of T were taken using 3 fs steps. Scanning \(-165 \text{ fs} < \tau < 252 \text{ fs}\) was sufficient for capturing all of the dephasing dynamics. For each value of τ, the echo signal was heterodyne detected using spectral interferometry by spatially overlapping it with a reference signal and dispersing the two pulses in a monochromator. The spectral interference fringes were detected using a 16-element LN₂-cooled HgCdTe array. The frequency \(\nu_3\) was scanned from \(2741 - 3890 \text{ cm}^{-1}\), while the pixel resolution in this configuration was approximately \(10 \text{ cm}^{-1}\) per pixel. The intensity of the reference pulse was 100 times less than that of the excitation pulses and preceded them in time by 700 fs. Given that no signal was observed in water even for \(\tau\) delays as short as 250 fs, any possible coherent reference-induced modulation of the sample is not present in the data. Finally, the 2D spectrum was obtained following a Fourier transform along \(\tau\).

To protect against long term drift or sudden fluctuations in laser power, all scans were taken within a strict “power window”. The intensity of the \(k_1\) beam was monitored with an InSb photodiode that was placed after the sample. The maximum allowable range was chosen to be ±2%, but typically ±1% was used. Since the echo signal varies as the cube of the electric field, and the heterodyne detected signal varies as the fourth power of the field, it is possible that 2% laser power fluctuations can produce 8 – 10% noise variations in the data. However, the observed amplitude noise was typically far smaller than this. Amplitude variations of spectral interference fringes were observed during successive 2D scans. These scan-to-scan variations were less than 2% under optimal experimental conditions. It can be assumed that the amplitude error in our 2D-IR data sets is no more than 3 – 4%.

Figure 6.1 shows a 2D-IR echo spectrum of H₂O, taken at \(T = 0 \text{ fs}\). All data in this section were taken using samples with 0.3 peak OD, with 500 μm thick CaF₂ sample cell

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The amplitude of the 2D spectrum is shown, for reasons that will be detailed later. There are two major features in the spectrum. This first is the slightly oval-shaped peak located just below the diagonal, near $\nu_1 = 3400$ cm$^{-1}$, $\nu_2 = 3450$ cm$^{-1}$. The second is the long ridge that extends along $\nu_1 = 3400$ cm$^{-1}$ down near $\nu_3 = 3000$ cm$^{-1}$. The latter feature is due to the $\nu = 1 \rightarrow \nu = 2$ excited state transition. This transition is hundreds of wavenumbers broad [146], and overlaps with the on-diagonal peak. The signal contributions to the on-diagonal peak are a combination of the fundamental $\nu = 0 \rightarrow \nu = 1$ transition and the well-known nonresonant electronic signal from the CaF$_2$ windows.

By $T = 50$ fs, the window signal will be much smaller than it is at $T = 0$ fs, therefore, most of the signal in Figure 6.2 is due to the water only. At $T = 50$ fs, the peak due to the water contribution appears almost exactly on the diagonal, as expected. Since the peak at $T = 0$ fs corresponds to a mixture of water plus window signal, it is shifted slightly off the diagonal because the centroids of the water and window signal contributions are different. There is also a reduction in the intensity of the off-diagonal excited state absorption peak, suggesting some decay of the $\nu = 1$ population even as early as 50 fs after excitation. The on-diagonal peak appears very slightly elongated, albeit in a direction about 30 degrees below the diagonal, not along the diagonal as would be expected for the case of an inhomogeneously broadened $\nu = 0 \rightarrow \nu = 1$ transition. This suggests that the window signal, although reduced in intensity by about an order of magnitude compared to $T = 0$, is still strong enough to influence the shape of the water peaks in the 2D spectrum.

To extract more information, the 2D spectra should be phased. Peaks in the amplitude spectra can be difficult to distinguish because all signals are positive, whereas in the absorptive spectra, the $\nu = 0 \rightarrow \nu = 1$ and $\nu = 1 \rightarrow \nu = 2$ transitions will have opposite signs, making it easier to distinguish the shapes of these broad, overlapping peaks. In order to do this, the window contribution needs to be subtracted from the overall signal, which involves phasing the 2D spectrum and subtracting the absorptive
Figure 6.1: 2D echo signal of H₂O in a CaF₂ sample cell at T = 0 fs. The magnitude of the nonresonant signal from the sample cell walls is comparable to that of the H₂O signal, with considerable spectral overlap between the two contributions.

and dispersive components separately. This is a very difficult problem. Water peaks that overlap with the window signal will shift their positions in the 2D spectrum depending on the magnitude of window signal that is subtracted off. The sample cell is positioned to maximize signal from the water, thus, the beam focus occurs near the focal plane of the water. In contrast, when the pulse is characterized using TG-FROG, the focal plane of the 500 μm thick window is used, which is shifted slightly from its position during the actual experiments. Thus, the magnitude of the CaF₂ signal can be approximated by taking a 2D spectrum with the window located within a few tens of microns of the sample cell’s actual position along the beam direction. The same can be done for the
Chapter 6. Two-dimensional infrared spectroscopy of pure liquid $H_2O$88

Heterodyned 2D-IR Spectrum of $H_2O$ using CaF$_2$ windows

$T = 50$ fs, Parallel Polarizations

Figure 6.2: 2D-IR echo signal of $H_2O$ in a CaF$_2$ sample cell at $T = 50$ fs. The nonresonant signal is reduced by about an order of magnitude compared to the $T = 0$ fs plot.

back window. However, the signals from the two windows will differ by more than a multiplicative factor. Because of the non-negligible OD of the sample between them, the nonresonant signal from the rear window will be generated by an excitation pulse that is spectrally modulated with respect to the pulse that generates signal from the front window. In this way, accurately simulating the signal from both sample cell windows becomes a computationally difficult problem.

Alternatively, one can multiply the window signal by a constant fitting factor and subtract it from the overall (sample plus window) signal such that the peaks from the sample contribution shift so that their corrected positions correspond to their expected positions in the linear absorption spectrum. This gives an acceptable cancellation of the
window signal for the proper choice of the fitting factor. This method was used to correct the 2D spectrum of acetic acid in Figure 4.8 by subtracting the peaks at $\nu_1 = \nu_3 = 2920$ cm$^{-1}$ and $\nu_1 = \nu_3 = 2990$ cm$^{-1}$ [109]. The cancellation becomes less accurate as one moves away from these central peaks in the 2D plot, because, as noted previously, the signal from the front and back windows are not proportional to one another. This method becomes less effective for eliminating the window contributions in the H$_2$O experiments because there are no such peaks that can serve as precise spectral benchmarks in the OH absorption spectrum. The uncertainty associated with trying to subtract off the window signal in this manner is too large.

Fortunately, optical methods of eliminating window signals do exist. As mentioned in Sections 3.2 and 3.3, certain beam polarization geometries can aid in eliminating on-diagonal signals in 2D-IR spectra. In the experiments presented above, the polarizations of $\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_{\text{ref}}$ corresponded to the angles ($0, 0, 0, 0$), measured relative to the plane of incidence. Zanni et al. suggested the use of the ($\pi/4, -\pi/4, \pi/2, 0$) polarization geometry for eliminating on-diagonal signals. In this case, the average over the orientations of the polarization-dependent transition dipole prefactors $< a_i b_j c_k d_l >$ will cancel in the on-diagonal tensor elements of the density matrix [71]. This will be true as long as the excited molecules are not rotating on a time scale comparable to the experiment. This is a sound assumption for water, since rotational motion takes place on 2.5 – 4.0 ps time scales [124, 131], while the maximum excitation pulse delays are only a few hundred fs. However, it will be shown in Section 6.3 that resonant energy transfer does take place on sub-100 fs time scales, and therefore the orientations of the excited dipoles will not remain constant on the experimental time scales considered here.

Using this crossed polarization geometry, the experiment was repeated, with all other experimental conditions the same as before. The 2D-IR spectra for $T = 0$ and 50 fs, are shown in Figures 6.3 and 6.4. The window signal, which is always on-diagonal, is reduced by about two orders of magnitude – a hugely significant reduction. The on-diagonal water
Figure 6.3: 2D-IR echo signal of H₂O in a CaF₂ sample cell at \( T = 0 \) fs using the crossed polarization geometry \((k_1, k_2, k_3, k_{\text{ref}}) = (\pi/4, -\pi/4, \pi/2, 0)\). The window signal contribution is nearly absent, and the water contribution appears as a single elongated peak along the diagonal, indicative of inhomogeneous broadening of the \( \nu = 0 \rightarrow \nu = 1 \) transition.

signal, i.e. the \( \nu = 0 \rightarrow \nu = 1 \) transition, is reduced by about one order of magnitude, while the off-diagonal excited state peak vanishes altogether. Since the polarizations of the first two excitation pulses \( k_1 \) and \( k_2 \) are orthogonal, the \( \nu = 0 \rightarrow \nu = 1 \) followed by the \( \nu = 1 \rightarrow \nu = 2 \) transition is no longer dipole allowed.

Nonetheless, at \( T = 0 \) fs (Figure 6.3), the \( \nu = 0 \rightarrow \nu = 1 \) transition appears with only a small distortion due to the window signal. It is clearly elongated along the diagonal, indicative of inhomogeneous broadening in the liquid. However, only 50 fs after excitation (Figure 6.4), the peak is no longer elongated, indicating a loss of inhomogeneity in the water structure on a 50 fs time scale. This suggests that the correlations in the
hydrogen bond network are lost in only 50 fs. In their rotational anisotropy study of H$_2$O, Woutersen and Bakker observed a sub-100 component of the anisotropy decay that they assigned to the modulations of the hydrogen bond network [139]. The present experiments are far more detailed in that we have used the 2D-IR method to directly observe the correlations and loss of inhomogeneity in the hydrogen bond network. Furthermore, it is crucial that the pulses used in this experiment are three times shorter than in the Woutersen work. In fact, our 70 fs pulses are considerably shorter than those used in any previous ultrafast study of H$_2$O. Thus, water dynamics can be resolved on faster time scales than in work previously reported by other researchers.

Despite the usefulness of the crossed polarization geometry in eliminating nonresonant
window signal, a better method is needed in order to more fully resolve all diagonal and off-diagonal features in the 2D spectra. The only way to eliminate the window signal for any polarization conditions is to construct a sample cell using windows that produce negligible signal in the first place. To meet this requirement, such a sample cell was built using nanofluidic, submicron-thick Si₃N₄ windows.

6.2 Si₃N₄ sample cells for the elimination of window signal contributions

As noted in the previous section, when the excitation pulses are fully or partially overlapped in time, nonresonant electronic signals can be observed in addition to the resonant nonlinear signal. In the case of the experiments considered here, with an H₂O sample held between CaF₂ windows, both nonresonant electronic and resonant echo signals are produced. Of course, the transparent CaF₂ windows will produce only the nonresonant electronic signal. Unlike the resonant echo signal, the nonresonant electronic signal is pulse width limited. If the relevant dynamics take place on a time scale much greater than the pulse width, then unwanted nonresonant contributions can be eliminated merely by observing the system when all three excitation pulses are no longer overlapped. This is precisely the approach taken by Asbury et al. in their study of HOD:H₂O [147]. Using 45 fs IR pulses to excite the OD stretch in HOD, they measured the 2D-IR spectra in a 12 : 1 dilution at various population times T, beginning with T = 125 fs. Considering that dephasing in the system was observed on a picosecond time scale, the excision of the first 125 fs after excitation is clearly not significant.

Furthermore, it must be re-emphasized that studies of isotopic water (such as the OH stretch in HOD:D₂O) lead to persistent correlations in the structure out to picoseconds (also see Sections 5.4 and 5.5). These prior experiments with HOD stand in stark contrast to what is observed in pure H₂O, where the dephasing is in the 50 fs range. In
other words, the water dynamics are taking place on a comparable time scale to the 60 fs pulse width. Therefore, elimination of nonresonant electronic signals by using excitation pulses that are well separated in time is not possible. The only way to observe a water echo signal that contains no electronic contribution is to eliminate the electronic contribution altogether. Given the comparable magnitudes of the window and water signals as depicted in Figure 6.1, this would require unreasonably thin CaF$_2$ or Sapphire windows. Decreasing the Sapphire window signal to the level of the noise floor in our data would require reducing the window thickness by about a factor of one hundred, down to a 2-3 micron thick Sapphire wafer. Even if such wafers were available, handling them and assembling a sample would be close to impossible without breakage.

On the other hand, thin windows made from Silicon Nitride (Si$_3$N$_4$) are commonly used in Transmission Electron Microscopy and X-Ray Microscopy [148]. Thin Si$_3$N$_4$ membranes have proved invaluable for mounting delicate samples. They can be fabricated as thin as 20 nm in order to minimize scatter, are chemically inert, and can be used over a wide temperature range (up to 1000°C). Furthermore, they are optically transparent from 200 nm through the entire mid-IR. With these advantages in mind, a sample cell was designed using Si$_3$N$_4$ membranes as a replacement for CaF$_2$ or Sapphire windows in an H$_2$O sample cell.

Tests were done using commercial products obtained from SPI Supplies [148]. It was key to work with the membranes in order to gauge their structural integrity and determine the most appropriate membrane thickness and area to use. The optical properties of the membranes were also tested in order to ensure their near 100% transmissivity and low scatter. The transmission at 3 μm wavelengths was essentially 100% with any membrane thickness, although with thicknesses greater than 800 nm, scatter was sometimes observed.

The main difficulty with using these cells was getting them to "wet", since Si$_3$N$_4$ is highly hydrophobic. Attempting to squeeze or trap water between the membranes
Figure 6.5: Design of Si$_3$N$_4$ nanofluidic cells.

was close to impossible. Treating the membrane surface with HF and H$_2$SO$_4$ solutions did improve the wetting somewhat, but it was still not nearly as hydrophilic as glass substrates. This necessitated switching to a custom membrane design, using a 10 nm SiO$_2$ layer on top of the Si$_3$N$_4$ in order to make the membranes more hydrophilic.

Regarding membrane thickness, it was found that membranes thinner than 200 nm or less tended to rupture quite easily during sample cell assembly. Also, thinner membranes tended to bulge outward once water was trapped inside, which, in the case of extreme bulging, led to irregularities in the sample thickness depending on the location of the focal spot. On the other hand, membranes that were too thick appeared less transparent to the eye, displayed etalon effects, and tended to scatter more light from the transmitted IR laser pulse. The best solution proved to be a 800 nm thick membrane, with a 2.0 x 2.0 mm$^2$ cross-sectional area, as depicted in Fig 6.5.

Figure 6.6 compares the nonresonant electronic signal from a 400 nm thick Si$_3$N$_4$ membrane with that from a 500 µm thick CaF$_2$ window. In both cases, the windows were positioned in the same focal plane. With $k_2$ and $k_3$ overlapped in time, $k_1$ was scanned, and the resulting signal (as a function of $\tau$) was recorded using a single channel InSb detector. It is evident in Figure 6.6 there was no measurable signal from the Si$_3$N$_4$ membrane, for the maximum possible signal must lie below the noise floor of the detector. The signal from the CaF$_2$ was at least three orders of magnitude larger. Note that this
is the minimum difference since the signal from Si$_3$N$_4$ membranes is so weak that it is beyond the sensitivity of the IR detectors. This drastic reduction in nonresonant signal clearly demonstrates the advantage of using Si$_3$N$_4$ instead of CaF$_2$ windows as sample cell window materials.

![Nonresonant Electronic Response in Sample Cell Windows](image)

Figure 6.6: Comparison of the nonresonant electronic signal for 400 nm Si$_3$N$_4$ membranes and standard 500 μm CaF$_2$ windows. Signal from the former is at least three orders of magnitude smaller than that from the latter, clearly demonstrating that the nonresonant window signals can be eliminated using Si$_3$N$_4$ nanofluidic cells.

There is also the nonresonant signal from the sample itself to consider. The water sample thickness was about a factor of three less than that of the Si$_3$N$_4$ membrane. However, the electronic polarizability of water [2] is a factor of 10 smaller than in Si$_3$N$_4$ [149]. This difference and the fact that the pathlength through the water region is three times shorter than that through the Si$_3$N$_4$ windows ensures that any nonresonant electronic signal from the water itself would be even smaller than the already negligible signal from Si$_3$N$_4$ shown in Figure 6.6. Therefore, low OD sample cells of pure H$_2$O in Si$_3$N$_4$ are expected to contribute negligible amounts of nonresonant nonlinear signal. It is certain that

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any light detected in the direction \( k_2 - k_1 + k_3 \) is genuine echo signal, free of unwanted nonresonant contaminations.

### 6.3 Transient Grating and polarization anisotropy experiments on \( H_2O \)

Using the \( Si_3N_4 \) sample cell windows, it is possible to construct thin \( H_2O \) samples suitable for femtosecond spectroscopy and detect echo signals that are not contaminated by nonresonant window signals. To the best of this author’s knowledge, this was the first application of nanofluidic sample cells in ultrafast IR spectroscopy. The peak OD of the samples for the following measurements was 0.2. The excitation pulses were 70 fs in duration and were centred at 3350 cm\(^{-1} \). Typical pulse spectra appear in Figure 6.7 superimposed upon the OH-stretch absorption. There is sufficient spectral content in the pulses to cover the entire OH-stretch region.

![Graph showing mid-IR pulse spectrum and OH absorption](image)

Figure 6.7: Typical spectra of mid-IR excitation pulses used in this experiment. The OH absorption spectrum (taken from [145]) is superimposed to indicate that the excitation pulses can cover the entire OH-stretch region.

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Figure 6.8 shows spectrally integrated transient grating measurements for population times $T$ up to 2 ps for both parallel and perpendicular polarizations of the probe pulse. The signals were homodyne detected using a single channel LN$_2$-cooled InSb detector. Both polarization directions exhibit a fast exponential decay with a 95-fs time constant, followed by a rise with a 1.3-ps time constant at later times $T$. The long time dynamics of the thermal rise is shown in the inset of Figure 6.8. This is due to ultrafast thermalization of the excitation, an effect that is expected due to the non-negligible temperature rise when working with very thin, low volume liquid samples [144, 150]. In addition, the steady state temperature rise in the H$_2$O sample was measured using an infrared thermal imaging camera, and was found to be 7 – 8°K. This means that heating of the sample is clearly insignificant, and the properties of the excited sample will not be appreciably different from that of room temperature water.

Using the TG signal for both parallel and perpendicular probe polarizations, the polarization anisotropy decay for water can be calculated. The anisotropy, $R(T)$, appears as a solid red curve in Figure 6.8, and reveals information about molecular reorientation and resonant energy transfer in the liquid. The polarization anisotropy in a pump-probe experiment is defined as

$$R(T) = \frac{a_\parallel - a_\perp}{a_\parallel + 2a_\perp},$$

where $R(T)$ is the anisotropy, and $a_\parallel, a_\perp$ are the absorption increases for the probe beam in the polarization directions parallel and perpendicular to those of the pump. The components of the TG signals we measure and display in Figure 6.8 are proportional to the square of the absorptions in Equation 6.1. Thus, the square roots of the TG components must be used when calculating $R(T)$.

The anisotropy decays exponentially with a 75-fs time constant. For comparison, the pulse width limited response is also shown in Figure 6.8. This shows that the very rapid decay of the polarization anisotropy is easily resolvable with the short excitation pulses that were used. As noted in Section 5.5, measurements in HOD mixtures have shown that
Figure 6.8: Transient grating signal and polarization anisotropy of H$_2$O. The parallel polarization (black line) and crossed probe polarization (blue line) data show a fast initial decay of the population, followed by a thermal grating rise due to vibrational relaxation on a picosecond timescale. The red curve is the polarization anisotropy $R(T)$, which decays exponentially with a 75 fs time constant. Dashed red line: pulse width limited response. Inset: longer time dynamics.

Reorientation takes place on picosecond time scales [124, 131]. Therefore, reorientation cannot account for sub-100 fs dynamics. The fast decay of $R(T)$ is due to energy transfer, in which the preferentially excited OH vibrations along the laser polarization direction can transfer their excitation to different water molecules via a resonant, nonradiative process [139, 151]. This will be discussed in further detail in Section 6.5.

Similar to the work by Woutersen [139], the anisotropy decay in a dilute 6:1 D$_2$O:H$_2$O mixture was also measured, also using the nanofluidic cell. The data appears in Figure 6.9 and is compared with the anisotropy decay in pure water. $R(T)$ for the HOD:D$_2$O mixture decays with a 700-fs time constant, about one order of magnitude slower than in pure water. This result is in agreement with the pump-probe measurements taken previously by Woutersen [139], but with 200-fs pulses they did not have sufficient time resolution...
Figure 6.9: Polarization anisotropy decay in pure water and in a 6:1 mixture of D₂O:H₂O. The dashed line shows the pulse width limited response. The solid red curve shows the 75 fs decay of the excited OH polarization anisotropy, while the green curve shows the far slower 700 fs decay of the D₂O:H₂O mixture. Both data sets were collected under the same conditions using nanofluidic cells.

The denominator of \( R(T) \) is known as the rotation-free signal and its decay is representative of the \( T_1 \) decay only [132, 152]. Thus, dividing the polarization signal difference \( a_\parallel - a_\perp \) by the rotation-free signal means that \( R(T) \) is sensitive to rotational reorientation and energy transfer only, and not to population decay. The \( T_1 \) lifetime can be determined by the rotation free term, i.e. \( S_{RF} = a_\parallel + 2a_\perp \), which is plotted in Figure 6.10. An exponential rise to the thermalization signal was fitted to both the \( a_\parallel \) and \( a_\perp \) components and subtracted off in order to produce the most accurate fit to the decay of \( S_{RF} \). This decay represents the \( T_1 \) relaxation time of H₂O, and was found to be 210 ± 25 fs, in reasonable agreement with the value of 260 fs found by Lock [144] using a two-colour pump-probe.
Figure 6.10: Rotation-free signal $S_{RF} = a_{||} + 2a_{\perp}$ as a function of $T$, in H$_2$O. The population time $T_1$, determined from the decay of $S_{RF}$, is 210 fs.

method. Their slightly higher value for $T_1$ is likely attributable to their longer (200 fs) excitation pulses, since the $T_1$ dynamics in water fall just within their minimum time resolution.

### 6.4 2D-IR echo of H$_2$O

The first heterodyne-detected TG and 2D echo experiments on H$_2$O will now be discussed. As was the case for the work presented in Section 6.1, the $\sim 1\mu$J excitation pulses were 70 fs in duration and were centred near 3350 cm$^{-1}$. Refer to that section for further experimental details. The peak OD of water in the Si$_3$N$_4$ sample cells was 0.2. Following a Fourier transform of the data along $\tau$, the data was phased by projecting the 2D spectrum along $\nu_3$ and fitting the result to the frequency-resolved pump-probe spectrum at the associated value of $T$ [75, 80].
Figure 6.11: Absorptive components of the 2D-IR echo spectra of pure liquid H$_2$O for different population times. Population times $T$ are a) 0 fs; b) 50 fs; c) 100 fs. The inhomogeneity indicated by the stretching of the positive peak along the diagonal in the $T = 0$ fs plot has almost completely decayed by $T = 50$ fs, clearly showing the very rapid dephasing and loss of memory in the system.
Figure 6.11 shows two-dimensional infrared spectra at different population times $T$. The absorptive component of the echo signal is plotted. At $T = 0$ fs, such spectra display an on-diagonal peak due to bleaching and stimulated emission of the $\nu = 0 \rightarrow \nu = 1$ transition and an off-diagonal absorption peak due to the $\nu = 1 \rightarrow \nu = 2$ transition. At $T = 0$ fs, the on-diagonal peak is stretched along the diagonal, indicating inhomogeneous broadening. The position of this peak is slightly shifted below the diagonal due to interference with the negative-going absorption peak [74]. This is unavoidable due to the considerable overlap between the very broad $\nu = 0 \rightarrow \nu = 1$ and $\nu = 1 \rightarrow \nu = 2$ transitions [146]. At $T = 50$ fs, this inhomogeneity is almost entirely lost (> 90% based on curvature of the line contours), and by $T = 100$ fs it is completely gone. The excited state off-diagonal peak decays on the same timescale. Most importantly, there are extremely fast processes that wash out the structural variations (inhomogeneous broadening), such that the OH stretching excitation loses its memory on extraordinarily fast timescales [153].

The full shape of the elongated on-diagonal peak at $T = 0$ fs is not completely resolvable in the data taken with the CaF$_2$ cells because of the considerable window signal. With all pulse polarizations parallel, clearly resolving this detailed peak structure was impossible. However, the rapid loss of inhomogeneity in Figure 6.11 is consistent with the data in Figures 6.3 and 6.4 because in the latter two figures the nonresonant signal was considerably reduced due to the crossed polarization conditions. But in contrast, the dynamics of the off-diagonal excited state absorption peak could not be observed with the crossed polarizations. Thus, the CaF$_2$ cell data is qualitatively correct and captured some of the essential dynamical features of the 2D spectra. It also provides a reliable consistency check for the data taken with the Si$_3$N$_4$ cell. In contrast, the Si$_3$N$_4$ cell data is completely free of any window signal, and therefore all relevant dynamical features of the $\nu = 0 \rightarrow \nu = 1$ and $\nu = 1 \rightarrow \nu = 2$ transition peaks can be observed for any polarization conditions and any population times $T$. Compared to CaF$_2$ or sapphire sample cells, the
advantages of the Si$_3$N$_4$ nanofluidic cells are now obvious.

The $\sim$ 50 fs decay of the off-diagonal excited state absorption peak in Figure 6.11 appears at first to be inconsistent with the homodyne TG data of Figure 6.10, which indicates a value of 210 fs for the excited state lifetime. To investigate further, the TG signal was heterodyne detected and spectrally resolved. Once more, the polarizations of all three pulses were parallel and the heterodyne signal was detected using spectral interferometry. $T$ was scanned from (-165, 400) fs in steps of 5 fs. The phasing was accomplished by taking frequency-resolved pump-probe spectra at several values of $T$ and performing a global fit of these to the corresponding slices along $\nu_3$ in the spectrally resolved TG data.

Figure 6.12 shows the absorptive part of the spectrally resolved transient grating signal. The contour scale is displayed from -1 to 1 in order to focus on the region of interest. At $T = 0$ fs, the positive peak corresponds to reduced absorption (bleaching) caused by the depletion of the $\nu = 0$ state of the OH stretching oscillator and stimulated emission from the $\nu = 1$ state. The negative peak corresponds to excited state absorption of the $\nu = 1 \rightarrow \nu = 2$ transition. The time evolution of the TG signals depends strongly on the spectral position. In order to accent these distinctions, spectral windows of the TG data were spectrally integrated and also plotted in Figure 6.12. The enhanced absorption below 3000 cm$^{-1}$ and the bleaching above 3500 cm$^{-1}$ display a very fast decay that is close to the 50-fs time resolution of our experiment. The net effect is a rapid spectral diffusion that sweeps the excitation toward the centre of the OH-band. A substantially slower decay is observed between 3170 and 3400 cm$^{-1}$ at the centre of the bleaching contribution. Thus, the heterodyned TG signal decays exponentially with a 95 fs time constant, corresponding to a $T_1$ decay of 190 fs ($\pm$25 fs). This is consistent with the result obtained in the homodyne detected results in Figure 6.10. This 95 fs decay is followed by the picosecond rise of the thermalization, which was also observed in the spectrally integrated data of Figure 6.8.
Figure 6.12: Absorptive component of the spectrally resolved transient grating signal of H$_2$O, plotted as a function of population time $T$. The main figure shows the fast spectral diffusion and excited state decay, and the beginning of the thermal grating rise. Normalized amplitude (Amp.) of the TG signal spectrally integrated in three windows, on the red (red line), middle (black line) and blue (blue line) sides of the spectrum.
There are also a number of subtler features in Figure 6.11 and Figure 6.12. A weak negative crosspeak appears near \( \nu_1 = 3000 \text{ cm}^{-1} \), \( \nu_3 = 3500 \text{ cm}^{-1} \) in the 2D-IR spectrum of Figure 6.12, with a matching feature at equivalent values of \( \nu_3 \) at negative \( T \) in Figure 6.11. Its corresponding crosspeak in the 2D-IR spectrum may be contained in the lobe in the upper left corner of the \( \nu = 1 \rightarrow \nu = 2 \) peak near \( \nu_1 = 3500 \text{ cm}^{-1} \), \( \nu_3 = 3000 \text{ cm}^{-1} \). The first crosspeak destructively interferes with the edge of the main \( \nu = 0 \rightarrow \nu = 1 \) peak in the 2D-IR spectrum. The crosspeak's amplitude is only about ten percent of that of the on-diagonal peak, which means that it is not distorting the shape of the latter peak in any significant way. These crosspeaks may represent a weak coupling between regions of very weak and very strong hydrogen bonding.

In general, the absence of obvious crosspeaks in the 2D-IR data is somewhat surprising. Symmetric stretch, asymmetric stretch and bend overtone regions of the OH-band are clearly visible in the \( \text{H}_2\text{O} \) Raman spectrum [112, 154] and in principle it should be possible to observe mutual coupling between these regions. Considering the very large homogeneous linewidth of the OH-stretch (observed in the work of Stenger et al. [136] and supported by the very fast dephasing observed here), these crosspeaks could be very difficult to distinguish because they are buried beneath the stronger on-diagonal peak. On the other hand, they may in fact be distinguishable at \( T = 100 \) fs, for their existence could account for the somewhat squarish shape of the on-diagonal peak in that 2D spectrum. Future experiments, likely involving a combination of better signal-to-noise as well as the crossed beam polarization geometries that were utilized in Section 6.1, will be necessary for establishing the full significance of these subtler features in the current 2D-IR data.
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6.5 Dephasing in liquid H₂O: The role of librations

Vibrational relaxation has been measured in many condensed media on time scales ranging from milliseconds (e.g. liquid O₂ at 70K [155]) to the subpicosecond time scales as observed in HOD:D₂O. In general, the rate of vibrational relaxation time depends on the number of accepting modes, their vibrational frequencies, and the energy gaps between the donor and acceptor modes. Besides the relaxation rate, determining the relaxation pathway is essential for understanding the structure of the molecules of interest.

Many vibrational relaxation mechanisms have been proposed for liquid water. For instance, Rey and Hynes were the first to propose (and perform calculations for) an intramolecular relaxation mechanism for HOD:D₂O mixtures in which energy is transferred from the OH stretch into the first overtone of the OH bend [121]. As is the case for the OH stretch, the bend overtone mode is also quite spectrally broad (the bend fundamental is 90 cm⁻¹ in breadth, while the overtone is believed to be about twice as broad) so the average frequency difference is about 200 cm⁻¹. The excess excitation energy would be deposited into low frequency solvent modes such as the translation modes below 200 cm⁻¹. The relaxation rate is expected to depend on the energy difference between the donating and accepting modes, a condition that was later examined experimentally by Gale et al. [125].

Another possible relaxation mechanism is that of pure relaxation. In this case, energy is transferred directly to the bath from the excited mode, such as the case for simple diatomic molecules like O₂ that have no other important solute modes. Woutersen and Bakker suggested that this was the mechanism responsible for the extremely rapid (sub-100 fs) anisotropy decay that they observed in pure H₂O (shown in Figure 5.5 and reference [139]).

Nonetheless, the dynamics observed in the present experiments are far more rapid than anything observed in all previous experimental and theoretical work with HOD:D₂O mixtures. The relaxation and dephasing processes in H₂O are more than an order of
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magnitude faster than in the isotopically substituted mixtures. In any HOD study, the excited vibrational transitions are not resonant with the surrounding bath molecules. Clearly, the situation is quite different when the OH excitation is resonantly coupled to the full hydrogen bond network as is the case in pure H2O. These drastic differences could not be predicted a priori based on the findings in the HOD:D2O systems studied to date [134]. In this light, how can this fast vibrational relaxation be explained? Stated differently, which molecular motions in pure water are fast enough to mediate changes in water structure on sub-50 fs time scales?

The frequency of an individual OH oscillator in the liquid depends on its local environment. From the X-ray diffraction data discussed in Section 5.2, it is clear that the local structure of water is highly disordered. These local substructures are modulated by the fluctuating network of intermolecular hydrogen bonds. These effects are responsible for the large (~ 250 cm⁻¹) inhomogeneous broadening of the OH stretch transition. Delocalization of the excitation only becomes appreciable when the coupling is comparable or greater than the inhomogeneity [156]. However, gas-phase studies of water clusters and theoretical calculations have shown that the coupling between OH oscillators is small compared to the disorder-related inhomogeneous broadening. This remains true even in ice, in which the hydrogen bond coupling is stronger than that in the liquid [157, 158]. Considering this, and the near-impulsive limit of the excitation pulses, we can think of the OH excitation as localized on a single oscillator, rather than delocalized over many oscillators. This excitation can then evolve in time due to intermolecular coupling mechanisms such as those mediated by dipole-dipole coupling and the hydrogen bond network.

From Figure 6.8, we observed a 75 fs decay of the polarization anisotropy. This decay can be due to either molecular rotation or excitation transfer between oscillators. These rotational relaxation times in liquids are in typically in the picosecond range [152], roughly increasing monotonically with increasing molecular weight [159]. In HOD:D2O mixtures, a value of 2.5 – 4 ps was assigned to the rotational relaxation time [124, 126].
This is nearly two orders of magnitude slower than the anisotropy decay measured in the present experiments, which indicates that the decay observed here must be due to excitation transfer. The transfer process is fairly rapid due to the close proximity between OH oscillators in pure water.

Furthermore, the initial value of the anisotropy in Figure 6.8 is 0.4. This is the expected value for a random initial distribution of OH oscillators with a linear transition dipole moment [160]. Given the volume of water traversed by the excitation beam as well as the energy in the laser pulse, only about two to three percent of the molecules are excited. On average, these excited molecules will be randomly distributed throughout the beam volume. The orientations of these excited molecules will also be random because, on average, they will be more than two correlation shells removed from their nearest excited neighbours. Therefore, the value of 0.4 for the anisotropy at \( T = 0 \) is the expected value, and one can assume that the excited oscillators are randomly oriented.

The excitation transfer from one excited OH vibration to a surrounding OH vibration will be dominated by dipole-induced dipole coupling in H\(_2\)O. There are higher order terms in the multipole expansion describing the electromagnetic coupling but the dipole term dominates the interaction. Under these conditions, the excitation transfer process can be characterized by a parameter called the Förster radius \( R_o \), which is defined as the distance between an excited and unexcited oscillator for which the rate of energy transfer is equal to the reciprocal of the excited state lifetime \( T_1 \) (assuming that the quantum yield \( \phi \) of the energy transfer process is unity). Equivalently, the Förster radius represents the separation distance for which the probability of excitation transfer to a neighbouring oscillator is equal to the probability of decay of the oscillator via a \( T_1 \) process (e.g. decay via intra or intermolecular modes). Thus, the Förster transfer rate \( k^{\text{Förster}} \) can be written as

\[
k^{\text{Förster}} = \frac{\phi \frac{R_0^6}{T_1}}{R^6}, \tag{6.2}
\]

where \( R \) is the separation distance between the excited molecular dipoles. It must be
noted that energy transfer can take place only while the $\nu = 1$ state is populated. In a two-level system, the lifetime of the $\nu = 1$ state is simply $T_1$, but for a multi-level system, this is not true in general because population can accumulate in intermediate states after the $\nu = 1$ state decays. Figure 6.12 shows that spectral diffusion leads to a blue shift of the $\nu = 1 \rightarrow \nu = 2$ transition toward the centre of the OH-stretch band. Because of the simultaneous red shift of the $\nu = 0 \rightarrow \nu = 1$ transition, the lifetime of the $\nu = 1$ state is not discernible in the TG data. The $T_1$ lifetime of $210 \pm 25$ fs from Figure 6.10 is consistent with the value of $T_1 = 190 \pm 25$ fs that was determined from the decay of the excitation in the spectrally resolved TG data of Figure 6.12, as well as the onset of the ground state recovery in that measurement.

For dilute mixtures of HOD:D$_2$O, in which the OH stretch is excited, the OH oscillators are too far apart for appreciably fast energy transfer to take place. Relations between the anisotropy decay and the excitation transfer time were first derived by Eisenthal [161]. Using Eisenthal's method, and accounting for the non-negligible rotational relaxation of the water molecules, the Förster radius in H$_2$O was estimated to be 2.1 Å by Woutersen and Bakker [139, 132], using the data that appears in Figure 5.5. From that value of the Förster radius, the energy transfer rate can be calculated. Taking $R = 2.8$ Å (the nearest neighbour O-O distance), and setting $\phi = 1$ (for the maximum possible transfer rate), we find $1/k_{Förster} = 5.6T_1$, which is far larger than the anisotropy decay time observed by Woutersen and in the present work. The $(R_0/R)^6$ dependence of the Förster process essentially ensures that this process will be considerably slower than the $T_1$ lifetime as long as $R_0 < R$. Woutersen recognized this and concluded that Förster transfer alone could not account for their observations in water. Instead, it was suggested that other energy transfer mechanisms were responsible, such as intermolecular interactions via the H-bond network, or higher order nonradiative transfer processes that are dependent on dipole-quadrupole or quadrupole-quadrupole interactions.

In Dexter's theory, the dipole-quadrupole coupling is predicted to be weaker in com-
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Comparison to the Förster transfer [162]. The Dexter coupling only acts as a fairly small correction to the Förster coupling. So if the molecules are close enough together such that this is not the case, then neither the Förster or Dexter expressions apply. In the multipole expansion for the electric field of the donor oscillator, the Förster expression assumes that only the dipole term is relevant. This is not true in the near field, because the charge distributions of the donor and acceptor dipole are close enough to overlap, which means that the OH's cannot be treated as point dipoles because the donor-acceptor displacement is comparable to the size of the dipoles themselves. In this case, it is likely inaccurate to assume that the intermolecular distance $R$ is equal to the O-O separation distance of 2.8 Å. Only when the dipoles are in mutually parallel alignment would it be strictly true to assume that $R = 2.8$ Å. For smaller separations, Equation 6.2 suggests that the transfer rate can become extremely fast. In principle, $R$ can vary both greater and less than 2.8 Å, depending on mutual orientations. The degree to which this happens is dependent on the short range order within the first correlation shell of water. But for dipoles that are not oriented parallel to one another, the Förster coupling is actually reduced [163]. The case where $R < 2.8$ Å also implies that the separation between hydrogen atoms in neighbouring molecules is less than the sum of their van der Waals radii, which will lead to a huge electrostatic repulsion between them. These orientations are obviously extremely unstable and will not be favoured in an equilibrium arrangement of water molecules [2, 164]. The short range ordering can be more fully quantified using the Kirkwood orientation parameter, which will be discussed below. All in all, a more general treatment of the energy transfer is necessary, which is beyond the scope of the present work.

When assuming that the polarization anisotropy represents the energy transfer time, as was the case in the studies by Eisenthal [161] and Woutersen [139], it must be true that the anisotropy decay represents the energy transfer time to water molecules oriented randomly relative to the dipole moment of the initial excitation. Thus, following resonant
excitation transfer, the newly excited acceptor molecule no longer contributes to the anisotropy. This is not true in general for a system with definite short-range correlations in its structure. As stated previously, we know that there are nearest neighbour position correlations in water from the X-Ray diffraction studies. A 7:1 dilution ratio of HOD:D$_2$O is close to the limit where the nearest OH's sit two correlation shells away from each other. The point dipole approximation applies to the OH oscillators at these separation lengths, thereby justifying the use of the Förster expressions to describe the energy transfer. For larger dilutions, such as those used by Woutersen for the Förster radius measurements, the nearest OH's sit further than two correlation shells from each other and their positions and orientations can be considered uncorrelated. However, for pure water, we know that the nearest neighbour O-O distance is highly correlated, suggesting that the dipole moments of neighbouring molecules are also correlated. In this case, on average, more than one sequential energy transfer event is needed to randomize the excitation. Thus, the 75 fs anisotropy decay should be considered an upper bound for the true energy transfer time in water.

The degree to which the short-range order in water affects this value can be approximated from the Kirkwood orientation parameter [165]. Kirkwood's theory is a model for the dielectric constant in ordered liquids. The Kirkwood constant, $g$, can be written as [165]

$$g = 1 + \sum_{i=1}^{N_i} < \cos \gamma_i >,$$

where $N_i$ is the number of molecules in the $i$th correlation shell, and $< \cos \gamma_i >$ is the average of the cosine angles $\gamma_i$ between the dipole moments of the central molecule with those in the $i$th shell. Thus, for a completely disordered arrangement of dipoles, $< \cos \gamma_i >$ equals zero and $g$ equals one. Typically, the ordering of molecules in a liquid is a short-range effect, meaning that the largest component of $g$ comes from the $i = 1$ contribution. For water, calculations have shown that the $i = 2$ contribution is about an order of magnitude smaller than that at $i = 1$ [2]. This is consistent with what one
would expect based on a straightforward comparison of peak heights corresponding to
the first and second correlation shells in the X-Ray diffraction experiments discussed in
Section 5.2.

The best estimates for $g$, as determined by both theory and experiment, are in the
2.6–2.9 range for H$_2$O at 0° C and decreasing as the temperature increases [166,167,168].
These theoretical estimates for $g$, as well as the interpretation of dielectric relaxation data
for water, tend to consider a tetrahedrally coordinated, two-component model for water
by using an ice-like arrangement of molecules in which each molecule can form either
zero, one, two, three, or four hydrogen bonds with its neighbours. The orientations of
hydrogen-bonded neighbours will be correlated with the central molecule, whereas non-
hydrogen bonded neighbours will not. As discussed in Chapter 5.4, more recent models
imply a more complex arrangement of orientations in which there is sizable dispersion
between the frequency of the OH stretch and the angle that the H-bond makes with
the O-O displacement vector [129, 130]. Thus, a full theoretical analysis of the problem
must take into account a more generalized range of possible bond and dipole moment
orientations. Nonetheless, the value of $g = 2.6 - 2.9$ is a more than reliable estimate for
the Kirkwood parameter.

In light of this fact, the decay time of the polarization anisotropy we observed is slower
than the actual resonant energy transfer time. The anisotropy is slower by a factor of two
or three in comparison to the decay that would be observed if there was no short-range
correlations in the dipole orientations. This reduces the energy transfer time from 75
fs to less than 50 fs, judging from the data in Figure 6.8. Recent quantum chemical
molecular dynamics simulations by Poulsen et al. support this assertion [169]. Using
harmonic potentials to characterize the normal modes of Ice Ih and water clusters, they
calculated energy transfer times as short as 50 fs for ice and 83 fs for liquid water. These
values are possibly overestimates because of the harmonic potential approximations that
were used but are in very good agreement with our observations.
Thus, the intermolecular resonant energy transfer process is still not fast enough to account for the loss of inhomogeneity observed in the 2D-IR data in Figure 6.11. One energy transfer event could average out the configuration over only one molecule in the first coordination shell. It is possible that energy transfer could average out the correlations in the water structure over many different molecules, but this would require many sequential transfer events, each requiring ~ 50 fs transfer times. In this case, the total time needed to sample all the neighbouring waters and account for the loss of inhomogeneity we observe in Figure 6.11 would be much larger than 50 fs. Similarly, an analogous argument can be made regarding the spectral diffusion as shown in Figure 6.12. Averaging over all the neighbouring waters in the first coordination shell results in the excitation frequencies being swept toward the centre of the OH band, which is the spectral diffusion that is observed. Resonant energy transfer is not fast enough to allow the excitation to sample all the surrounding water molecules and account for these observations.

The fact that the dephasing process is so much faster than the energy transfer demonstrates that it is the librations, or hindered rotations of the water molecules, that largely determine the hydrogen bond potential and energy distribution in the hydrogen bond network [153]. The assignment of dephasing processes on sub-100 fs femtosecond time scales to librational motions is not a new concept. For example, Luzar and Chandler, in their theoretical work on hydrogen bond dynamics [170, 171], assigned the fast initial decay of the hydrogen bond time correlation to librational coupling. Similar conclusions appear in work by Tanaka and Ohmine [7], as well by Saito and Ohmine [172] in their MD simulations of the $\chi^{(3)}$ response of water. However, the means of observing such fast dynamics has not been possible until the development of sub-100 fs mid-IR sources in recent years.

Experimentally, the connections between the spectral density of states of liquid water and its molecular motions were made decades ago [112]. Optical heterodyne detected Raman-induced Kerr Effect spectroscopy in the work of Palese et al. [173] as well as Cast-
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ner et al. [174] have also assigned the sub-100 fs components of the third-order response function in water to librational motions. The other potential candidates with respect to microscopic motions that could possibly explain the observed dynamics are all too slow to account for the observations. Low frequency translational modes corresponding to hindered translations (≈ 60 cm⁻¹) and hydrogen bond stretching modes (≈ 100 - 200 cm⁻¹) all have periods of hundreds of femtoseconds and are much too slow to account for the dynamics reported here. The bending mode, at 1650 cm⁻¹ has a ~ 20 fs period with a spectral width of ~ 50 cm⁻¹. This is several times smaller than the width of the OH stretch. Therefore, coupling of OH-stretch to the OH-bend cannot account for the rapid spectral diffusion that occurs throughout the entire OH-stretching band. The microscopic motions must involve the librational modes in the 300 - 1000 cm⁻¹ range, with periods ranging from 30-90 fs. Only these hindered rotations about the three axes of water are fast enough with periods in the correct range to account for the observed dephasing and spectral diffusion processes.

Librations rapidly modulate the length of the excited OH-bond, spreading the excitation amongst the neighbouring water molecules. The spectral diffusion in Figure 6.12, that is, the sweeping of the OH frequencies toward the centre of the OH band, is a direct result of this spatial averaging of the excitation. The net effect is a lowering of the energy of the ν = 1 level, thereby blue shifting the ν = 1 → ν = 2 transition and red shifting the ν = 0 → ν = 1 transition. This effect is qualitatively similar to the spectral shifts associated with electronic solvation [175, 176]. In such experiments, shifts in the time-resolved fluorescence occurs due to charge rearrangement following electronic excitation. In comparison, the motions of electronic charges following vibrational excitation are quite small. The vibrationally excited OH is only 0.1 - 0.2 Å longer than the relaxed OH, with the O-O separation changing by about the same amount [177]. So, the spectral diffusion observed in the water data is not a result of charge rearrangement, but rather, it is the result of hydrogen bond network rearrangement. This leads to the loss of structure cor-
Figure 6.13: Schematic energy-level depiction of structural relaxation in H$_2$O. Librations rapidly sweep the $\nu = 1 \rightarrow \nu = 2$ transition toward the blue and the $\nu = 0 \rightarrow \nu = 1$ toward the red. This is accompanied by rapid modulation of the hydrogen bond lengths (represented by the slow mode coordinate $Q$) in the vicinity of the excited molecule.

relations between neighbouring molecules. Similarly, in the work cited above, librations were assigned to be the mechanism driving the electronic solvation process, for they are the only modes fast enough to modulate the motion of charges on the time scale of the observed spectral diffusion.

This process is depicted schematically in Figure 6.13. For schematic simplicity, harmonic energy levels were drawn (albeit anharmonically displaced). Upon initial excitation, the minimum of the $\nu = 0$ level occurs at a higher value of the slow mode coordinate $Q$ than the $\nu = 1$ level. The same is true of $\nu = 1$ with respect to $\nu = 2$. Following excitation, rapid modulation of the OH-stretch frequency by the librations results in modulation of the H-bond network and thus a shift of the vibrational energy levels of the water molecule with respect to $Q$. As was discussed previously, $Q$ and the OH-stretch frequency are monotonically related [129, 130, 131]. Reduction in the energy difference between $\nu = 0$ and $\nu = 1$ is a consequence of the shift of the $\nu = 1$ level along the slow mode coordinate (right side of Figure 6.13). The excited molecule relaxes and the surrounding H-bond network homogenizes in that the energy minima of $\nu = 0, 1, 2$ line
up at nearly equal values of the slow coordinate $Q$.

The TG data seems to show a faster decay on the red side of the OH band compared to the blue. It has been suggested that the vibrational $T_1$ lifetime displays a frequency dependence [178, 179], in which larger hydrogen bond-induced redshifts of the OH-stretch frequency relative to the gas phase value lead to faster $T_1$ relaxation times. Although the fastest (sub-50 fs) dynamics that are observed are due to librational motions, we cannot completely rule out other relaxation processes, such as vibrational relaxation via the bend overtone mode, that are distinct from those induced by the librational coupling and operate on slower time scales. Such competing processes must necessarily take place via short-lived intermediate states that will subsequently contribute to the ground state recovery. For instance, $T_1$ relaxation of highly red-shifted OH's via the bend overtone would lead to a faster net decay rate (when compounded with the effects of librational coupling) on the red edge of the TG spectrum in comparison to the blue edge, which is in fact what is observed. In addition, the fast librational modulation of the spectrum could very well display its own frequency dependence, resulting in spectral diffusion times that are dependent on excitation frequency. This was precisely what was observed by Steinel et al. with respect to spectral diffusion of the OD excitation [128]. The spectral width along a chosen $\nu_1$ of the $\nu = 0 \rightarrow \nu = 1$ peak in the 2D-IR spectrum is known as the dynamic linewidth and the frequency dependence of the spectral diffusion can be inferred from this by making this measurement at various waiting times $T$. A thorough consideration of a frequency-dependent $T_1$ lifetime must be properly weighted by this effect. However, if a frequency dependent spectral diffusion takes place on approximately the same timescale as a frequency dependent $T_1$ lifetime, separating these two effects is extremely difficult. Furthermore, the extremely rapid loss of correlation in pure H$_2$O (Figure 6.11) in comparison to the isotopic mixtures means that it is not possible to make observations over a large enough range of $T$ in order to properly measure the dynamic linewidth, at least not with the time resolution that is currently possible using state of
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the art femtosecond IR laser sources.

Let us now continue examining the differences between the present work with H₂O and previous work with isotopic mixtures. The HOD molecule in D₂O or H₂O represents a very different system compared to either pure liquid. For HOD:D₂O, there are several possible vibrational relaxation pathways that do not exist in bulk H₂O [142]. The HOD molecule contains an OH stretch frequency ν₀H ~ 3400 cm⁻¹, an OD stretch frequency ν₀D ~ 2500 cm⁻¹, and an HOD bend δHOD ~ 1830 cm⁻¹. Of course, relaxation via librational modes, i.e. intermolecular ν₀H → low frequency (libration + translation/H-bond) modes is one possible pathway. The other possible intermolecular relaxations are ν₀H → ν₀D, ν₀D → 2δD₂O, and ν₀D → δD₂O. The possible intramolecular relaxations are ν₀H → ν₀D (distinct from the intermolecular process involving the same vibrational energy pathway), ν₀H → δHOD, and ν₀H → 2δHOD.

In H₂O, the situation is quite different. The bend overtone 2δH₂O is located within the OH stretching band, thereby affecting the spectral character of the OH stretch via Fermi coupling [107, 109, 125]. Other than ν₀H → low frequency modes, the only other relaxation pathway is ν₀H → δH₂O (both intra and intermolecular). These extra relaxation channels are responsible for the differing dynamics between HOD:D₂O and pure H₂O. Similar arguments can be made for HOD:H₂O, in which the OD bond is excited. The highly localized OH bond in HOD:D₂O is exceedingly different from the OH bond in H₂O that is resonantly coupled to the surrounding solvent. Since the excited and localized OH does not resonantly sample the extended H-bond network, population relaxation of the OH is a much slower process.

Another analogy can be made with the electronic solvation process. A lone ion surrounded by solvent molecules can be thought of as a “defect” in the liquid. There are no resonant interactions between the surrounding solvent molecules and the solute. The response is solely driven by electrostatic interactions in which the ensuing relaxation is described as a repolarization of the nonequilibrium solute-solvent structure into a new
equilibrium distribution that is distinct from that of molecules in the bulk liquid. In a similar manner, a lone HOD molecule surrounded by H$_2$O or D$_2$O molecules can be considered a "defect" in the hydrogen bond and librational networks. The HOD molecule is effectively decoupled from the solvent. Part of the response of the surrounding H$_2$O or D$_2$O to the excited HOD mode will be driven by changes in the electrostatics with the slightly larger bond displacements and weaker H-bond (depending on relative orientations of the surrounding water). But in the case of pure H$_2$O, the excited OH mode becomes fully resonant with surrounding OH modes through the various stochastic motions that modulate the hydrogen bond network and OH frequency spectrum. In addition, during the crossings at which the OH mode is fully resonant, dipolar couplings will lead to larger amplitude exchanges in relative OH displacement with the surroundings. This interaction leads to loss in phase information encoded in the excited OH by the excitation pulse.

The net effect is that coupling coefficients of the excited OH mode to the bath fluctuations are much larger for pure water than for HOD. The coefficients describing the degree of coupling between the bath fluctuations and the excited H$_2$O modes will have a resonant enhancement and a corresponding increase in the degree of modulation of the OH frequency spectrum by the surrounding solvent fluctuations. Since the $\nu_{OH} \rightarrow$ low frequency modes decay pathway in HOD:D$_2$O or HOD:H$_2$O is off-resonant, then the other relaxation pathways listed above – all of which occur on the timescale of hundreds of femtoseconds due to the large energy differences involved – will strongly contribute to the observed dynamics. Relaxation via the $\nu_{OH} \rightarrow$ low frequency modes can still occur, but the effect is much weaker than in the case of pure H$_2$O because of the off-resonant coupling [180]. This accounts for the fast librational component that has been observed in some of the HOD:D$_2$O experiments by other groups [138]. The slower components they observe are all due to alternate relaxation pathways – none of which exist in pure H$_2$O. These statements need to be followed up by rigorous theoretical modelling of the water interactions for pure H$_2$O. This effect will likely provide one of most rigid tests for

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improving our potential basis states for water.

Very recent theoretical [181] and experimental [182] work on water in confined environments such as reverse micelles also demonstrates the profound differences between bulk water and small ensembles of water molecules. As the micelle sizes decrease, increases in the $T_1$ lifetime are predicted and observed. In other words, smaller water nanopools curtail the spatial extent of the H-bond and librational network, effectively isolating the excited OH oscillator and resulting in the expected lengthening of the vibrational relaxation time. These studies may also have significant contributions from interfacial water that is difficult to cleanly separate from those of the bulk water. Irrespective of this, the spatial extent of the hydrogen bond network has a profound effect on the correlations and dynamics of liquid $\text{H}_2\text{O}$.

The dephasing rates in pure water are more than an order of magnitude shorter than in the HOD mixtures [127, 128, 138, 183]. In the 2D-IR work by Steinel, in which the OD stretch in $\text{HOD}:\text{H}_2\text{O}$ was excited, the 2D spectra show elliptical features indicative of inhomogeneous broadening that persist out to 1.6 ps [128], whereas in the present work the spectral features are nearly symmetrical after only 50 fs. Similar dephasing time scales are observed in the HOD:$\text{D}_2\text{O}$ experiments. The present work conclusively demonstrates that pure $\text{H}_2\text{O}$, in which all pathways interconnecting the different degrees of freedom are coupled within the hydrogen bond network, is a fundamentally different physical system than the isotopic mixtures, in which the OH is highly localized within the solvent.

6.6 Conclusions

The work presented in this thesis has answered some long-standing problems regarding the ultrafast dynamics of the hydrogen bond network in water. The origins of the anomalously broad OH-spectrum of water is one of the oldest unsolved problems in spectroscopy,
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dating back at least to the 1930’s, to the Raman studies of Cross et al. [10]. Contemporary with the first X-ray work of Morgan and Warren [11], a rough sketch of water began to emerge. These early studies found that water molecules formed tetrahedral structures, with each molecule forming up to four hydrogen bonds with its neighbours. Models of the hydrogen bonding in water go back even further to the 1920 work of Latimer and Rodebush, in which they were seeking an explanation for water’s high dielectric constant [12]. However, it is only recently, with the development of femtosecond infrared laser sources and 2D-IR spectroscopy, that it has become possible to move beyond the analysis of static spectra and probe the changes in water structure on the timescale of molecular vibrations.

The main findings in this thesis are as follows. 2D-IR echo spectroscopy was able to distinguish between the static and dynamic contributions to the OH-stretch vibration in water, thereby providing direct insight into the structure and dynamic behaviour of the hydrogen bond network. The frequency of the OH stretching excitation in H$_2$O loses its memory on 50 fs time scales, indicative of extremely fast processes that wash out the structure correlations in the hydrogen bond network on extraordinarily fast time scales. The net effect is a very efficient redistribution of energy within the hydrogen bond network. These dephasing mechanisms are faster than those observed in any other liquid.

Fast librational motions (hindered rotations) are the relevant excitations that mediate these very rapid dephasing processes. Librational coupling is also the mechanism behind the spectral diffusion in H$_2$O, as evidenced by an extremely fast sweep in the OH frequencies on a 50 fs time scale.

Population relaxation with a 190 ± 25 fs $T_1$ decay time was also observed. Finally, the time scale of resonant excitation transfer between OH-oscillators in H$_2$O was characterized. This sub-100 fs energy transfer contributes to the loss of memory and spectral diffusion that is observed, but it is not fast enough to dominate the process. Rather, the
librations, with periods between 90 and 30 fs, are the only excitations with periods in the relevant time range to account for all of the observed dynamics.

There are profound differences between the results in the present work, which examines pure H$_2$O, and similar studies of isotopic mixtures such as HOD:D$_2$O. In the HOD studies, the vibrational excitations are highly localized within the surrounding hydrogen bond network, leading to dynamics that are more than an order of magnitude slower than the results reported here using H$_2$O. In contrast, the present work has examined the fully resonant problem in which all dynamical pathways are interconnected.

In this respect, this thesis work should serve as an experimental benchmark with respect to refining the water potentials that are currently used by the theoretical community. A large variety of basis sets for water have been used over the years, ranging from rigid single point charge models to those incorporating flexible potentials and more complex charge distributions. Most models can accurately predict certain macroscopic properties of water such as its density and molecular diffusivity. In this respect, with many forms of the potential describing certain macroscopic properties equally well, it is difficult to discern which models offer the most appropriate description of water.

Theoretical descriptions of the ultrafast dynamics of water have faced similar challenges. Calculations by Corcelli et al. [184] showed that the frequency-frequency correlation functions (FFCF) for the OH-stretch in HOD:D$_2$O are nearly identical when either single point charge or polarizable potentials are used. The most significant differences between the two models occur within the long (> 1 ps) decays of the FFCF. In addition, the FFCF’s for the OD-stretch in HOD:H$_2$O are quite similar to those for the OH-stretch in HOD:D$_2$O, also with little quantitative differences between the two drastically non-identical models. However, as noted in Chapter 5 of this thesis, the FFCF’s obtained experimentally for both liquids are noticeably distinct from each other [127, 138, 147, 183]. All of this evidence suggests, as noted by Corcelli, that the models themselves are incomplete when it comes to describing the ultrafast dynamics of water. When most of these
model potentials were first devised, they were parameterized to obtain the best fit to the macroscopic properties of water. In this respect, it is not particularly surprising that they should fail to highlight the differences in femtosecond dynamics between isotopic mixtures of water, as well as differences between those isotopic mixtures and pure H$_2$O. Therefore, our work should be invaluable to the theoretical community with respect to improving upon the existing potential functions for water so that macroscopic properties as well as microscopic dynamics can be accurately simulated to give a complete molecular level description of the many body potential of liquid water.

The results obtained in this thesis also allow us to better understand the shortcomings of certain calculation methods. For example, as described in Section 5.4, Rey and Hynes attempted to calculate the $T_1$ relaxation time of HOD:D$_2$O. They performed a Molecular Dynamics simulation using a flexible point-charge model for D$_2$O. They found $T_1$ times that were far longer than those measured in later experiments on HOD:D$_2$O or on H$_2$O in this thesis. As discussed in Chapter 5, their method assumes a strict separation of time scales. For instance, it is assumed that rotational relaxation is much faster than vibrational relaxation, which means that rotations can be treated in equilibrium with the bath and can be treated classically, while the vibrations are treated quantum mechanically. This thesis work has shown that there is no separation of time scales between the relevant dynamics. The time scales of the dephasing, resonant energy transfer, OH-stretch and H-O-H bend vibrational lifetimes are all in the 100-fs range or less [185], indicating a need for a fully anharmonic basis set for water.

Very recent theoretical work may have profound implications on further understandings of liquid water. Using a full Quantum Dynamics and Molecular Dynamics approach, de la Peña and Kusalik have have found evidence for a very significant quantum rotation effect in the hydrogen atom displacements [186]. Classically, D$_2$O and H$_2$O are practically identical [187], but quantum mechanically, different spatial distributions of the oxygen atoms emerge, leading to quantum tunnelling effects past the classical turning points in
the many body potential of water. This would increase the RMS librational motions beyond what is predicted classically, leading to notably distinct relaxation dynamics between D\(_2\)O and H\(_2\)O. These effects are more pronounced at low temperatures (less than 20\(^\circ\)C and into the supercooled region of water) and differences in the dynamics of bulk and deuterated water should be observable using 2D-IR methods.

In addition, DeVane et al. have derived new methods of calculating nonlinear response functions that involve quantum corrections to classical correlation functions [188]. This is necessary in order to incorporate quantum mechanical dipole effects into the classical correlation functions that are needed for performing molecular dynamics simulations. Their work placed specific emphasis on modelling the 2D-Raman and 2D-IR spectra of liquids [188], and their results for the density of states and 2D-IR spectra of water are encouraging.

Water plays a central role in biology, and therefore, in all life on this planet. On the molecular level, it is absolutely necessary to understand water in order to make sense of even the most basic biological processes. Since the 1950's, it has been generally agreed that the hydrophobic principle is the most significant energetic factor responsible for the folding of proteins [189]. Non-polar molecules will tend to aggregate when placed in an aqueous environment because it becomes energetically favourable to arrange themselves in this manner. It is entropically unfavourable for water molecules to arrange themselves and form hydrogen bonds around the solute. Rather, the solute molecules will aggregate, thereby casting many water molecules back into the bulk. This minimizes the ordering of the water molecules in contact with the surface of the solute, leading to an increase in entropy and a decrease in the Gibbs free energy of the system. In this way, hydrophobicity can be a driving mechanism for determining the structure of polypeptide and nucleic acid chains. It also plays a role in stabilizing the three dimensional structures of these molecules [190, 191].

Of course, water in the presence of such biomolecules will not be identical to pure,
bulk H\textsubscript{2}O. In particular, the first few layers of water molecules adjacent to the surface of a non-polar solute should show effects related to the presence of the solute. The dynamics of biomolecules are sensitively dependent on the solvent environment, which is almost always H\textsubscript{2}O. In order to understand the influence of H\textsubscript{2}O on the biomolecular structure and dynamics, it is essential to understand the structure and dynamics of bulk H\textsubscript{2}O. These are exactly the issues that have been solved in this thesis.

Reorientation dynamics of biomolecules (including, for example, protein folding) are also highly dependent on details of the interactions between the molecule and its solvent. It follows that water dynamics can depend upon the nature of the biomolecular solute. For instance, Russo et al. examined diffusion rates and rotational dynamics of water molecules in the presence of a hydrophobic amino acid chain [192]. Using quasi-elastic neutron scattering, they studied the dynamic behaviour of the water molecules as a function of the amino acid concentration. As expected, both diffusional and rotational motions of water are slowed with increasing solute concentrations. It is encouraging that biologists are gaining new understandings of water’s active role in stabilizing protein structures [191]. Such research strongly suggests that water’s unique ability to rapidly stabilize itself via its rapidly modulating H-bond network is important for helping stabilize biomolecules [190, 193]. In nucleic acid chains, for instance, the hydrophobic effect leads to shielding of the hydrophobic base pairs within the hydrophilic sugar-phosphate backbone. This effect, along with the hydrogen bonding between nucleic acid base pairs, is responsible for stabilizing the extended structure of the entire molecule.

Proteins cease to function below a certain hydration threshold [192]. Once the solute concentration exceeds this threshold, it can be assumed that the dynamics of the water molecules have slowed below a threshold that is necessary for maintaining the stability of the protein. From these examples, it is clear that a full description of these biological processes must include a thorough characterization of bulk H\textsubscript{2}O on femtosecond time scales – including the intricate role of its hydrogen bond network – in order to fully
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comprehend the structure and function of complicated biomolecules. As such, this thesis work is key to understanding the dynamics of liquid water on a molecular and atomic level.

This research opens the door for a considerable amount of follow-up work. The diffractive optics setup can be used for heterodyned nonlinear spectroscopies throughout the mid-infrared. Applications of the Si3N4 cell are certainly not limited to water samples and can be used in conjunction with any nonlinear optics experiment that requires elimination of nonresonant signals.

Immediate future work would entail a more complete examination of the 2D-IR echo of H2O. A temperature dependence is an obvious extension of this work. Heating the water sample will result in a weakening of the hydrogen bonds and the temperature-dependent 2D-IR spectra should reflect these changes. Also of interest is the region below ambient temperature, between 0 - 25°C. The density maximum is located within this region, as well as the most drastic temperature dependent changes in the heat capacity. These properties should also be reflected in the dynamics of the hydrogen bond network. Ice is expected to exhibit very different behaviour, although fabricating such a thin sample of solid ice presents a formidable technical challenge. Finally, as mentioned previously, a comparative study of pure D2O can highlight how quantum effects can impact the molecular dynamics.

In relation to the above discussion of water’s key role in biology, it will be necessary in future studies to look at water dynamics in actual chemical environments. The behaviour of molecules and ions in aqueous solutions is of considerable important in biochemistry. The properties and structural reconformations of macromolecular structures will sensitively depend on their aqueous environment. This will further motivate femtosecond time-resolved studies of the behaviour of water in ionic [194] and cellular [195] environments. These 2D-IR spectroscopies can also probe the structure and dynamics of complicated macromolecules in aqueous environments. For instance, Fang et al. have re-
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Recently performed 2D-IR on isotopically labelled α-helices and have shown how 2D-IR can acquire details about conformations of the α-helix in the vicinity of the tagged isotopomer by observing the dephasing rates that it undergoes in its aqueous surroundings [196].

All of these exciting new avenues in femtosecond biochemistry show that physicists and chemists are beginning to realize the power of an entire field of new spectroscopic techniques. A considerable amount of groundbreaking work is surely yet to come.
Bibliography


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