The structure and structural dynamics of hydrogen bonded liquids were studied experimentally and theoretically with coherent two-dimensional infrared (2DIR) spectroscopy. The resonant intermolecular interactions within the fully resonant hydrogen bond networks give access to spatial correlations in the dynamics of the liquid structures. New experimental and theoretical tools were developed that significantly reduced the technical challenges of these studies. A nanofluidic flow device was designed and manufactured providing sub-micron thin, actively stabilized liquid sample layers between similarly thin windows. A simulation protocol for nonlinear vibrational response calculations of disordered fluctuating vibrational excitons was developed that allowed for the first treatment of resonant intermolecular interactions in the 2DIR response of liquid water.

The 2DIR spectrum of the O-H stretching vibration of pure liquid water was studied experimentally at different temperatures. At ambient conditions the loss of frequency correlations is extremely fast, and is attributed to very efficient modulations of the two-dimensional O-H stretching vibrational potential through librational motions in the hydrogen bond network. At temperatures near freezing, the librational motions are significantly reduced leading to a pronounced slowing down of spectral diffusion dynamics. Comparison with energy transfer time scales revealed the first direct proof of delocalization of the vibrational excitations. This work establishes a fundamentally new view of
vibrations in liquid water by providing a spatial length scale of correlated hydrogen-bond motions.

The linear and 2DIR response of the amide I mode in neat liquid formamide was found to be dominated by excitonic effects due to largely delocalized vibrational excitations. The spectral response and dynamics are very sensitive to the excitonic mode structure and infrared activity distributions, leading to a pronounced asymmetry of linear and 2DIR line shapes. This was attributed to structurally different species in the liquid characterized by their degree of medium range structural order. The response is dominated by energy transfer effects, sensitive to time-averaged medium range structural order, while being essentially insensitive to structural dynamics. This work is the first to recognize the importance of energy transfer contributions to the 2DIR response in a liquid, and provides additional proof of the well-structured character of liquid formamide.
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This work was possible only through three very fruitful and productive collaborations, providing many opportunities to meet technical and scientific challenges, work in different scientific and cultural environments and significantly broadening the scope of this work. The experiences of working at the Max-Born Institute (MBI) in Berlin, Germany, are invaluable to me, characterized by the intensity and excitement of a high-time-pressure experimental setting. The four-foot-long piece of foam (just not big enough) to sleep on under the laser table after 24-hour experimental sessions will not be forgotten - ever. The work at the MBI was possible only for and excelled through the numerous contributions from Thomas Elsaesser, Erik Nibbering and Nils Huse. I am deeply grateful for the opportunity to work with and learn from them, in particular the latter which I did plenty of.

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I am grateful for the guidance provided by my Ph. D. committee: John Sipe, Aephraim Steinberg, as well as John Wei and Gregory Scholes. Their critical questioning of my thesis work helped greatly in better defining the questions and focus of this work. I also want to thank Paul Brumer and his group, in particular Ignacio Franco, for a number of helpful discussions and numerous advice.

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List of Acronyms

2D  two-dimensional
2DIR  two-dimensional infrared
2PE  two-pulse photon echo
3D  three-dimensional
3PE  three-pulse photon echo
BBO  $\beta$-barium borate
BOE  buffered oxide etch
CPA  chirped pulse amplification
CNF  Cornell Nanoscale Facility, Cornell University, Ithaca, NY
DFG  difference frequency generation
D-bond  deuterium bond
DNA  deoxyribonucleic acid
DMF  dimethylformamide
DO  diffractive optic
ESA  excited state absorption
ESE  (induced) excited state emission
FA  formamide
FCF  frequency correlation function
fs  femtosecond
FTIR  Fourier transform infrared
GSB  ground state bleach
H-bond  hydrogen bond
HTG  heterodyne transient grating
IR  infrared
LO  local oscillator
LENS  European Laboratory for Nonlinear Spectroscopy, Florence, Italy
LPCVD  low pressure chemical vapor deposition
MA  magic angle
MBI  Max-Born Institute, Berlin, Germany
MCT  mode coupling theory or mercury cadmium telluride (see context)
MD  molecular dynamics
NISE  numerical integration of the Schrödinger equation
NMR  nuclear magnetic resonance

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<table>
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<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>OPA</td>
<td>optical parametric amplifier</td>
</tr>
<tr>
<td>OPLS</td>
<td>optimized potential for liquid simulation</td>
</tr>
<tr>
<td>PA</td>
<td>polarization anisotropy</td>
</tr>
<tr>
<td>PEPS</td>
<td>photon echo peak shift</td>
</tr>
<tr>
<td>PECVD</td>
<td>plasma enhanced chemical vapor deposition</td>
</tr>
<tr>
<td>PP</td>
<td>pump probe</td>
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<tr>
<td>PPS</td>
<td>pump probe spectroscopy</td>
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<tr>
<td>ps</td>
<td>picosecond</td>
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<tr>
<td>RIE</td>
<td>reactive ion etching</td>
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<tr>
<td>SNR</td>
<td>signal-to-noise ratio</td>
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<td>SOS</td>
<td>summing-over-states</td>
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<td>TDC</td>
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Citations to Published Work

Parts of this thesis include research work already published in the following papers:


In preparation:


Conference proceedings:


International conference presentations, oral:


Chapter 1

Introduction

The structure and structural dynamics of molecular liquids, and in particular hydrogen bonded (H-bonded) liquids, is characterized by the complex interplay of molecular structure, strength and anisotropy of the intermolecular forces, as well as fluctuations thereof. In particular the complex dynamics encountered in liquid systems make predictive experimental and theoretical studies very challenging, often much more challenging than solid or gaseous state research. The most important reason for this discrepancy is the inapplicability of otherwise common and very helpful separation of time scales-approximations. The intermediate regime of intermolecular interactions causes continuous interplay between all degrees of freedom in the liquid structure.

One could expect, though, that these microscopic peculiarities are not important for most situations with real life relevance, and that simple pictures of liquids based on macroscopic and statistical measures could be sufficient to describe most phenomena. In this picture, the particularities of the local molecular structure, interactions, and dynamics are averaged out, leaving no detectable trace for scientists to be concerned about. While this is certainly true for many cases, a large number of the simplest odd phenomena in H-bonded liquids remained a mystery over centuries and could only be explained from the microscopic details of H-bonding interactions and dynamics. The most prominent
example is the density maximum of liquid water at 4°C and the low density of ice [1, 2]. Moreover the role of H-bonded liquids, in particular for water, in facilitating biological processes critically relies on microscopic oddities of the intermolecular interactions [3].

Despite having recognized the importance of the microscopic liquid behavior, the field remained poorly understood and explored until ~10 years ago mainly due to a lack of experimental and theoretical techniques sensitive to the liquid structural dynamics whose important processes happen on picosecond (ps)-time scales. Up until then, techniques sensitive to the time-averaged structure were the main source of information. Neutron and X-ray diffraction are the most prominent structure determining methods [4, 5]. Alternatively, optical and in particular vibrational linear spectroscopies can report on structure through the modulation of the vibrational potentials from the particular local structural arrangement [2]. In this sense, the frequency of the vibrational chromophore directly reports on the local structural environment. These linear studies are however mostly sensitive to the time-averaged structure determined by the harmonic parts of the intermolecular potentials, whereas the liquid dynamics are driven by intermolecular anharmonicities [6].

With the recent advent of ultrafast laser sources, an entirely new field of study emerged that makes it possible to monitor the liquid dynamics in real time with the use of time-ordered ultrashort laser pulses [7]. The temporal resolution of these time-resolved experiments has now reached the regime of the fastest liquid dynamics. Additionally, the most recent advances in ultrafast spectroscopy include coherent multidimensional spectroscopy [8–10]. These experiments can probe not only vibrational energy redistribution and relaxation caused by the anharmonic terms in the intermolecular potential, but are also sensitive to dephasing of vibrational excitations. In the two-dimensional infrared (2DIR) spectroscopy approach, this dephasing of coherent vibrational motion can be used to monitor the evolution of vibrational frequency correlation, which in turn reports on structural dynamics and relaxation in real time [11–13]. This very exciting discovery
has triggered a whole new field of investigations.

While still young, the field is rapidly maturing and several recent discoveries show that the direct link between vibrational frequency and local structure does not always hold [14–17]. In these cases, the spectroscopy measurements are not only influenced by structural dynamics, but also by the particular properties of the vibrational potentials and their interaction with the liquid environment. Several different scenarios occur in which the spectroscopic results have to be investigated thoroughly in order to recover the desired structural information. On the other hand, some of these scenarios might also provide additional information on structural correlations in the liquid - if understood and interpreted properly.

Pure H-bonded liquids are one of these cases. Here, resonant vibrational interactions between neighboring molecules are the major additional component distorting the direct interpretation of the spectroscopic results [15, 16]. Vibrational excitations can then occur delocalized over many chromophores, a phenomenon referred to as the formation of vibrational excitons [8]. Most 2DIR studies have intentionally avoided this additional complexity by using isotopic substitution [18–27]. This way, the direct frequency-structure relation could be recovered. However, this approach necessarily only gives a localized probe of the structural dynamics, whereas the long range correlations in the H-bond networks are central to understanding the special properties of these liquids.

This doctoral thesis is devoted instead to explore 2DIR spectroscopy of neat liquids thoroughly - to embrace the complexity added by resonant couplings as a direct probe of medium range correlations. The resonant intermolecular interactions provide additional information on the structural dynamics in H-bonded liquids, in particular on spatial correlations involved in structural fluctuations. It is found that the length scales of these correlations are extremely sensitive to the particularities of the vibrational potentials and the intermolecular interactions.

The work in this thesis focuses on two hydrogen-bonded liquids, water and formamide.
These liquids display quite different regimes of structure, structural dynamics and resonant vibrational interactions, allowing a general assessment of the 2DIR spectroscopic features encountered in neat liquids. The work includes experimental and theoretical studies. For both parts, new tools were developed that now make these studies easily accessible for the scientific community. A number of new features were discovered in which it could be shown that indeed 2DIR studies of neat liquids are highly sensitive to spatial correlations in the liquid structure and structural dynamics, information that is not accessible with any other technique to date.

The introductory Chap. 2 and 3 provide the necessary background on the objects and the methods of this study, respectively: H-bonded liquids and nonlinear vibrational spectroscopy. The 2DIR experimental details are described in Chap. 4, focussing on the nanofluidic technology developed as a central part of this work. Chap. 5 presents the main experimental results of this thesis: the temperature dependence of the 2DIR spectrum of liquid water. Chap. 6, 7, and 8 contain the theoretical part of the dissertation. Chap. 6 describes the simulation protocol, specifically developed to treat resonant vibrational coupling. The first application was made to study the 2DIR spectrum of liquid water in Chap. 7. Chap. 8 investigates the 2DIR spectrum of liquid formamide, in which the vibrational excitations are largely delocalized. A short general discussion is given in Chap. 9, and this work is concluded in Chap. 10.
Chapter 2

Structural Dynamics in Hydrogen Bonded Liquids

This introductory chapter will discuss some fundamental physical properties of liquids and hydrogen-bonded (H-bonded) liquids in particular. Traditionally, liquids are characterized by their thermodynamic behavior, that is by time-averaged macroscopic observables. It has been a long standing goal in physical chemistry to qualitatively and quantitatively connect these thermodynamics to the microscopic structure and the associated dynamics. It is the complexity of intermolecular interactions in liquids that has made this task an extremely challenging one. This chapter gives a very brief general overview and some details regarding the H-bonded liquids studied in this work, water and formamide.

2.1 A Brief Theory of Liquids

The liquid state is commonly defined through its distinction from other states of matter, most importantly the solid and gaseous states. Transitions between the different states of matter are achieved by changing the density and/or the temperature of the substance, which can be related to the distance dependence of the intermolecular forces and
Chapter 2. Structural Dynamics in Hydrogen Bonded Liquids

their fluctuations, respectively. Distinction between liquid and solid states is relatively straightforward and can be simplified to three major points:

1. Long range structural order. Crystalline solids (not all solids) exhibit long range structural correlations, a phenomenon never found in liquids. Structural disorder is of central importance for liquids.

2. Shear resistance. Solids usually react elastically to shear stress, liquids do not and will flow instead. The most important quantity for this phenomenon is the shear viscosity, relating the stress to the change in flow.

3. Self diffusion. This can be understood as the probability of molecules switching positions, which is several orders of magnitude higher in liquids than it is in solids.

The distinction between liquid and gas phase is somewhat more subtle, both are generally described as fluids. Due to the existence of a critical point for most substances, it is always possible to continuously transfer between the two states, making a clear distinction difficult. Under normal conditions though, the density is certainly the best quantity to identify the state, usually being several orders of magnitude higher for liquids than for gases. As a consequence, the atoms or molecules experience different distance regimes of the intermolecular forces for the two states of matter. This is particularly important for molecular liquids since here the liquid phase intermolecular interactions show very complex, anisotropic behavior due to the specific molecular structure in close proximity. A typical liquid phenomenon not present in gases is surface tension.

Liquid theory focuses on two microscopic quantities, the so-called (partial) pair distribution function \( g(R, \Omega) \) (combining the radial \( R \) and the angular \( \Omega \) distribution for molecular liquids) [28] and the density time correlation function \( F(k, t) = \frac{1}{N} \langle \rho_{-k}(0) \rho_{k}(t) \rangle \) [29]. Whereas \( g(R, \Omega) \) fully characterizes the time-averaged structure of the liquid, \( F(k, t) \) represents fluctuations and is usually expressed in reciprocal space \( (k) \) to analyze the different length scales involved in structural fluctuations. It is the goal of liquid theory to
connect these microscopic properties to macroscopic (often thermodynamic) observables, to provide a consistent theoretical description of the liquid state.

Information on microscopic structures is commonly acquired from diffraction experiments, namely X-ray and neutron diffraction [28]. Experimental data is gathered in reciprocal space and Fourier transformed to get the pair distribution functions. For molecular liquids, the (partial) structure factors (sensitive to the molecular structure only) are of particular importance. Extraction from experimental data is more delicate and is usually only achieved from series of X-ray and neutron scattering experiments. For larger molecules, nuclear magnetic resonance (NMR) [30] experiments are useful to get the molecular structure factors.

A great deal of theoretical work has focused on deriving expressions for $F(k, t)$, generally referred to as Mode-Coupling Theory (MCT) [29, 31, 32]. Even though the techniques and approaches within MCT vary widely, the general idea is to solve the equation of motion for $F(k, t)$ by investigating the coupling between different modes of the density fluctuations characterized by their wave vector $k$. In particular, liquid-glass transitions were investigated intensely, where glasses are identified through the non-vanishing asymptotic value of $F(k, t)$, i.e. a remnant of structural correlations over very long time scales despite strong fluctuations [32].

The ultimate goal of liquid theory is to derive the intermolecular potential that can reproduce the macroscopic and microscopic, time-averaged and dynamic behavior of the liquid.

2.2 The Hydrogen Bond

Hydrogen bonding (H-bonding) [3] is a strong intermolecular interaction of type $A - H \cdots B$, where $A$ and $B$ are electronegative atoms such as nitrogen, oxygen and fluoride. The hydrogen atom $H$ is covalently bound to the donor atom $A$, the other atom $B$
 Chapter 2. **Structural Dynamics in Hydrogen Bonded Liquids**

acts as the *acceptor*. The H-bond is mostly electrostatic in origin, a result of partial charging of the donor and acceptor as well as the hydrogen atom itself. Since the partial charges often lead to large static dipole moments, H-bonds are dominated by dipole-dipole interactions. The bond also exhibits some covalent character; it is highly directional and can upon bond formation modulate the acceptor and donor receptivity of forming more H-bonds, allowing for the creation of H-bond networks.

After its first postulation in the 1920’s by Pauling and others [33, 34], it took several decades until the importance of H-bonding in biological systems was fully realized. It is the intermediate strength of the bond (strong compared to other intermolecular forces, weak compared to most intramolecular bonds), that makes it so versatile. While strong enough to stabilize double helix structures storing the genetic code in DNA [35], it is also weak enough to allow opening of this double helix during cell division [36]. The structure of most polypeptides and proteins is a result of H-bonding, such as formation of the $\alpha$-helix [37] and the $\beta$-sheet [38]. Most importantly to this work, almost all biological processes take place in liquid water [1, 2] which owes most of its unique properties to H-bonding. Similarly, the interaction of water with biological molecules in facilitating biochemical reactions is orchestrated by H-bonds.

Traditionally, H-bonds are classified by the average strength of the bond. Molecular liquids, like water and formamide investigated in this work, have *weak* H-bonds with $\approx 4 – 10$ kcal/mol binding energy [2, 39, 40]. Medium strong H-bonds with bond energies of $\approx 10 – 40$ kcal/mol are found in many molecular complexes, for instance between base pairs in DNA or in acetic acid cyclic dimers [41]. Strong H-bonds are usually found in molecular crystals. The strongest ones are symmetric with the hydrogen in the center of the donor and the acceptor and can for instance be found in water ice at high pressures. Some examples of H-bonded systems are shown in Fig. 2.1.

The weak H-bonds in liquid water and formamide have dissociation energies comparable to the thermal energy $kT$ at ambient conditions. This results in frequent bond
breaking and reformation events on ps time scales \cite{24,42}. However, since the close molecular packing in the liquid phase prevents a full dissociation in most cases, it is not uniquely defined whether two molecules are H-bonded or not. Much discussion about the definition of the H-bond can be found in the literature. Often a simple cutoff length of the $A - H \cdots B$ configuration is used to separate the bound from the unbound state \cite{19,43}. Since also the angle of the bond (angle between $A - H$ and $H \cdots B$) has a strong impact on the bond strength \cite{44}, angular cutoffs are also common \cite{45}. However, no such rigorous definition is unique, and discussions about average numbers of H-bonds and also dynamics of certain H-bonded species should always be seen in the light of the

Figure 2.1: Schematic representation of some typical H-bonded systems. (a) Cytosine-Guanine base pair in DNA. (b) Acetic acid dimer \cite{41}. (c) Formamide, unit cell in the 2D crystal structure \cite{5}. (d) 3D H-bond network in liquid water, from Parinello group. Dashed lines represent the H-bonds.
respective ambiguous H-bond definition.

2.3 Microscopic Structure

The microscopic structure of liquid water has been discussed in great detail recently [46]. In the following only a brief overview is given with emphasis on comparing structural properties of liquid water and formamide.

Liquid H$_2$O

The atomic level structure of the water molecule has been extensively studied [1, 2]. The oxygen atom shares two of its valence electrons with the hydrogen atoms, to form two strong covalent $O - H$ bonds, with an equilibrium bond length of $\approx 0.96\text{Å}$ for the isolated molecule. The characteristic angle of $104.5^\circ$ [2] between the two $O - H$ bonds arises from balancing the electron densities between the bound and the unbound oxygen valence electrons. The unbound valence electron densities are pushed to the backside of the molecule upon $O - H$ bond formation. Due to the large electronegativity of the oxygen, the sharing of the bound valence electron densities is not equal, their magnitude being larger and more localized on the oxygen. This results in significant partial charges (positive for the hydrogen, negative for the oxygen) that lead to the large static dipole moment of the water molecule of 1.85 D [47].

The water molecule can form up to four H-bonds, two as donor from each $O - H$ and two as acceptor. With the small size of the H$_2$O molecule, this results in liquid water having the highest density of H-bonds per unit mass of any substance. Ultimately, it is this high density of H-bonds that is responsible for many of the unique properties of the liquid, such as the large heat capacity and the density maximum at 4$^\circ$C [48]. Its low viscosity of 0.89 mPas at room temperature [47] is also directly related to the H-bonding, since the rapid breaking and reformation of the weak H-bonds reduces the
Due to the four possible H-bonds, water assumes a tetrahedral structure in its most common crystalline solid form, hexagonal ice (ice I) [2]. Much discussion can be found in the literature about the time-averaged structure of liquid water [49–55]. Findings and interpretations based on diffraction experiments and molecular dynamics (MD) simulations range from intermediate size fully crystallized domains [49], via the average tetrahedral structure in the first solvation shell [52–54], to reduced tetrahedral arrangements even in the first solvation shell [55]. The most commonly accepted and experimentally supported picture is summarized in Fig. 2.2. An isosurface of radial oxygen-oxygen distribution is shown. The major peaks for the first solvation shell (first neighbor) are the fairly localized distributions from donated H-bonds. The acceptor side is somewhat washed out from fluctuations. While long range order is lost, some significant residual tetrahedral arrangement is maintained in the first solvation shell and, less pronounced, in the second solvation shell. Even though intra- and intermolecular motions blur out the distribution functions, their structure and anisotropy is not completely lost up until the third solvation shell.

**Liquid Formamide**

Formamide (FA, HCONH$_2$) is a common organic solvent; its derivative dimethylformamide (DMF, HCON(CH$_3$)$_2$) is even more frequently used. FA is the smallest molecular unit containing a peptide bond (R-C(=O)-N(H)-R) and is produced from ammonia ($NH_3$) and formic acid (HCOOH). The reaction between the carboxyl group (RCOOH) and the amine group (:$NRRR$) forming the peptide bond by releasing water is one of the most important reactions in organic chemistry. It is a crucial step in creation of polypeptides and proteins from amino acids. The $N\cdot C=O$ group is often referred to as an amide group.

The lowest energy molecular structure of FA is planar as seen in Fig. 2.3, with all
Chapter 2. Structural Dynamics in Hydrogen Bonded Liquids

Figure 2.2: The (a) radial and (b) spatial oxygen-oxygen pair distribution functions of liquid water. (a) Radial distribution function of water ice and liquid water at two temperatures acquired from neutron diffraction experiments. Reproduced from Soper et al. [52, 56] (b) Isosurface of the spatial oxygen-oxygen distribution, reproduced from Kusalik et al. [54]

Figure 2.3: The isolated formamide molecule. It is the smallest molecular unit containing a peptide bond.

atoms including the three hydrogens lying in one plane. The hydrogens are often labelled cis \((H_1)\), trans \((H_2)\), and amide \((H_3)\) hydrogens following their molecular arrangement with respect to the \(C=O\) carbonyl bond.

FA can form up to four H-bonds, two with the \(N-H\) bonds acting as donor and two with the oxygen as acceptor. In its solid phase, FA has a monoclinic crystal structure and forms a two-dimensional (2D) H-bond network in-plane with the molecular plane [5, 57].
The unit cell of the 2D crystal contains four FA molecules and is shown in Fig. 2.1 (c). The 2D crystal exhibits two major features, cyclic dimers and zigzag chains. The cyclic dimer H-bonds are formed by the cis hydrogens and tend to be somewhat weaker than the trans H-bonds creating chains [5, 58]. In principle, one additional H-bond with the C-H as donor is possible. This H-bond is significantly weaker (~4 times) than the N-H···O bonds [59], and is not evident in the crystal structure.

The liquid state of FA, even though far less studied than liquid water, is also subject to extensive discussions in the literature [5, 58, 60–66]. Despite most recent proposals [62], it is generally believed that the two-dimensional nature of the H-bond network is preserved also in the liquid phase. The now emerging picture of the liquid state of FA predominantly consists of extended H-bonded chains or zigzag chains with a minor presence of ring-shaped oligomers [64]. Thus, FA is often referred to as a well structured liquid [66]. Recent theoretical studies [62] alternatively suggest a 3D H-bond network in FA similar to liquid water, but are not supported well by experiments.

Due to the time-averaged nature of the common structure-determining diffraction experiments, no conclusive picture of instantaneous structures or structural dynamics and relaxation times can be drawn directly. Traditionally, the understanding of the dynamics is gained from MD computer simulations. The common strategy is to assume some intermolecular potential, perform the MD simulations and then compare the statistics, such as the pair correlation functions, with diffraction experiments and thermodynamical properties. The (often empirical) potentials are then refined based on these time-averaged observables. However, the intrinsically predicted dynamics that are crucial to chemical reactions could not be tested against experiment, simply due to the lack of time-resolved structure determining experiments. As a typical problem arising as a consequence, MD simulations often fail to describe temperature dependence of the observables [67]. One of the most important reasons for this failure is the insensitivity of the diffraction results
to anharmonicities in the intermolecular potentials. It is these anharmonicities, however, that drive the dynamics in the liquid phase and are responsible for highly temperature dependent phenomena.

In order to resolve this predicament, experiments sensitive to the structural dynamics down to the femtosecond (fs) time scale are highly desirable to explore the anharmonic parts of the intermolecular potentials. However, accessing dynamic structural information on the ps or even fs-time scale is not an easy task. The most prominent structure determining experimental techniques based on X-ray and neutron diffraction or NMR have not yet achieved the necessary time resolution and measure time averaged structures. Only very recent efforts in both time resolved electron diffraction [68, 69] and X-ray diffraction [70, 71] techniques, as well as most recent time resolved X-ray absorption measurements [72] seem promising in being able to resolve some of the fastest structural dynamics in the liquid phase in the near future. These new experiments now use nanofluidic technology developed as part of this work, see Sec. 4.4.1.

2.4 Structural Fluctuations and Vibrational Spectroscopy

Traditionally, static and dynamic structural information has been acquired using optical and infrared spectroscopies. In particular, mid-infrared (mid-IR) frequencies of intramolecular vibrations reflect, similar to the magnetic moments in NMR, the local chemical and structural environment. The distribution and dynamics of local structures then define the spectroscopic observables, through modulation of the intramolecular vibrational potentials from structural evolution. In principle, linear spectroscopic observables recorded in the frequency domain contain the full dynamical information. In the liquid phase, this is however largely obscured by the many contributing processes and the generally large line widths, making it virtually impossible to deconvolve the linear response.
In this respect, the use of nonlinear spectroscopies with time-ordered ultrashort pulses allows access to the different regimes of structural dynamics directly in the time domain. In principle, there are two distinct regimes of the IR response allowing two different ways to access the intermolecular potentials: intramolecular vibrations (~ 4000 – 1000 cm$^{-1}$) and intermolecular motions (< 1000 cm$^{-1}$).

Direct spectroscopic access to the intermolecular motions is challenging. While linear spectroscopies such as far-IR and Raman again only probe the harmonic parts of the potential, nonlinear experiments in this frequency range are extremely difficult, mainly due to technical reasons. A few brave attempts have been made using 2D Raman spectroscopy [65, 73–75]. In particular the work of Li et al. [65] further supports the findings of FA being well structured even in the liquid phase. Nonlinear Terahertz (THz) spectroscopy is currently being developed [76] and promises to give direct information on low-frequency anharmonic motions in neat liquids in the future.

The intramolecular vibrations of the isolated (gas phase) water and FA molecules are schematically depicted in Fig. 2.4. An overview of the fundamental transition frequencies of these modes is given in Tab. 2.1. The highest frequency modes (~ 3600 cm$^{-1}$) are the \textit{O-H} and \textit{N-H} stretching motions which in gas phase split into the a(nti)symmetric ($\nu_{as}$) and the symmetric ($\nu_s$) mode of the two \textit{X-H} bonds. In the gas phase, the respective transition dipole moments of the symmetric and asymmetric stretches are perpendicular. The vibrational motions are in-plane with the molecular planes which is the case for all intramolecular modes discussed here. The next lowest frequency mode is the \textit{C-H} stretch in FA at ~ 2800 cm$^{-1}$. Important vibrations in the 1500 – 2000 cm$^{-1}$ region are the bending motion ($\delta$) in water and the amide I and II modes in FA. The amide I mode is mostly \textit{C=O} stretch (therefore also referred to as carbonyl stretch) with some \textit{C-H} bending and \textit{C-N} stretching contribution. The amide II in FA is mostly a \textit{HNH} bending, or scissoring mode, also with some \textit{C-N} stretching contributions [2, 77]. Both amide modes are typical for peptide bonds and, even though structurally slightly different
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Water

![Diagram showing intramolecular vibrations in water](image1)

- $v_3$: asymmetric OH stretch
- $v_1$: symmetric OH stretch
- $v_2$: HOH bend

Formamide

![Diagram showing intramolecular vibrations in formamide](image2)

- $v_1$: asymmetric NH stretch
- $v_2$: symmetric NH stretch
- $v_3$: CH stretch
- $v_4$: C=O stretch, amide I
- $v_4$: HNH scissor, amide II

Figure 2.4: Intramolecular vibrations in water and formamide in the gas phase. The corresponding infrared transition frequencies are given in Tab. 2.1. Only the five highest frequency modes for formamide are shown. The arrows indicate the direction of the respective transition dipole moments.

in each system, are present in all peptides and proteins.

Upon H-bonding interactions in the liquid phase, the intramolecular bands shift in frequency and broaden. Both effects occur as a consequence of a multiplicity of ef-
Table 2.1: Intramolecular vibrations in water and formamide, gas and liquid phase, frequency shifts and peak broadening upon H-bonding. For formamide only the five highest frequency intramolecular modes are given. Water data taken from [2], all frequencies given in cm$^{-1}$. Formamide data from [60, 78–80]. *CH stretching mode in liquid FA shows a well resolved substructure with four dominant peaks [78]. The vibrational modes are illustrated in Fig. 2.4. All frequencies are given in cm$^{-1}$.

<table>
<thead>
<tr>
<th>substance</th>
<th>mode</th>
<th>description</th>
<th>gas phase</th>
<th>liquid width</th>
<th>shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>$\nu_3$</td>
<td>$\nu_{as}(OH_2)$</td>
<td>3755</td>
<td>$\sim 3400$</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>$\nu_1$</td>
<td>$\nu_s(OH_2)$</td>
<td>3656</td>
<td>1645</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>$\nu_2$</td>
<td>$\delta(HOH)$</td>
<td>1594</td>
<td>1645</td>
<td>-50</td>
</tr>
<tr>
<td>formamide</td>
<td>$\nu_1$</td>
<td>$\nu_{as}(NH_2)$</td>
<td>3570</td>
<td>$\sim 3300$</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>$\nu_2$</td>
<td>$\nu_s(NH_2)$</td>
<td>3448</td>
<td>2888</td>
<td>-30</td>
</tr>
<tr>
<td></td>
<td>$\nu_3$</td>
<td>$\nu(CH)$</td>
<td>2855</td>
<td>2888</td>
<td>-25</td>
</tr>
<tr>
<td></td>
<td>$\nu_4$</td>
<td>amide I</td>
<td>1755</td>
<td>1685</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>$\nu_5$</td>
<td>amide II</td>
<td>1580</td>
<td>1600</td>
<td>-30</td>
</tr>
</tbody>
</table>

effects: H-bonding induced weakening and strengthening of intramolecular bonds, fast H-bond fluctuations and resonant vibrational couplings. It is these modifications of the vibrational bands that allows access to structural information and dynamics through vibrational spectroscopy. The IR spectra of liquid water and FA are shown in Fig. 2.5.

In both systems, the highest frequency $O-H$ and $N-H$ modes are most sensitive to the H-bonding mainly due to the small mass of the hydrogen atom. In both liquids, these stretching bands red shift and broaden by several hundred wave numbers as the H-bond with the $X-H$ acting as donor weakens these bonds. Since the H-bonding is usually not symmetric, the symmetric/asymmetric character of the vibrations is washed out, an effect that is further amplified by resonant vibrational couplings. Additionally, the H-bonding leads to a significant increase in the transition dipole moments for these transitions which also scales with the strength of the H-bonds. In a similar manner, the anharmonicity of the $X-H$ vibrational potentials increases with the H-bonding strength. The high sensitivity to H-bonding and the generally strong absorption has lead to the most extensive studies of these stretching bands. The exact microscopic origin of the lineshapes and widths in structure and structural dynamics has been subject to much
discussion and is a central question within this work. In particular the $O-H$ stretching mode in liquid water will be discussed in great detail in Chap. 5.

The $C-H$ band in FA behaves very differently and is studied much less in the literature compared to the other modes in the liquid. A blue shift of $\sim 30 \, cm^{-1}$ is observed in the liquid phase compared to the gas phase, and the line remains relatively narrow. Since the $C-H \cdots X$ H-bonds are weak and not evident in the solid or liquid structure, the small frequency shift of the $C-H$ band is interpreted to be a result of shortening and stiffening of the $C-H$ and the $C-N$ bond due to the other H-bonds of the molecule [81]. If $C-H \cdots X$ H-bonds are formed, they are likely to be highly transient leading to fluctuation induced broadening of the band [26].

The amide I mode in FA is particularly interesting. A red shift and broadening occur

![Linear IR spectra of liquid water and formamide. Reproduced from ref. [82] and [80], respectively.](image)

Figure 2.5: Linear IR spectra of liquid water and formamide. Reproduced from ref. [82] and [80], respectively.
upon H-bonding, but much less than for the $N-H$ and $O-H$ stretching modes. With the weight of the oxygen, the $C=O$ weakening due to acceptance of H-bonds by the oxygen and the resulting red shift of the band is reduced. Simultaneous stiffening of the $C-N$ additionally counters this effect. As will be discussed in great detail in Chap. 8, the majority of the lineshape and likely even parts of the red shift is caused by resonant vibrational coupling with neighboring peptide bonds.

Finally, the $HOH$ and $HNH$ bending modes again behave similarly in both liquids. They exhibit a mild blue shift upon H-bonding, likely caused by the geometrical constraints of the bending motions from the H-bonds donated by the $X-H$ bonds. Due to the relative weakness of both transitions, resonant vibrational coupling is also less pronounced. The exact origin of the IR lineshapes of these modes is, however, not well explored in the literature.

The two modes investigated in this work, $O-H$ stretch in water and amide I in FA, are also the most studied in the literature. This is in part due to their accessibility since both bands are the strongest transitions in the respective liquid. However, the structural information that is gained from both modes is significantly different. The $O-H$ stretch is most sensitive to the immediate environment through the H-bond donated by the $O-H$. This local probe of the liquid structure is even more strongly emphasized by isotopic substitution, for example $OD/ND$ stretching mode in $HOD$ and $HCONHD$ dissolved in $H_2O$ and $HCONH_2$, respectively [18–25]. These substitutions not only prevent resonant vibrational couplings, but also localize the stretching vibrations on one bond only. As a consequence, the $OD/ND$ stretching frequency is almost entirely determined by one H-bond (or rather D-bond) - the most local structural probe. The amide I band in FA but also in polypeptides and proteins, however, is most sensitive to larger length scales of structure since the band shape is dominated by resonant vibrational couplings leading to formation of vibrational excitons [14, 60, 81, 83–99].
2.5 Vibrational Excitons

The expression *exciton* is widely used for electronic and vibrational excitations that can be treated as elementary excitations or *quasiparticles* [8]. Originally, excitons were discovered in crystalline semiconductors and insulators where electrons and holes can form a bound state through coulomb interaction, and are classified as either Frenkel [100] or Mott-Wannier [101] excitons. Often such excitons form about impurities and structural distortions or in semiconductor nanostructures, where the geometrical constraints define the properties of the excitonic wave functions. In this sense, electronic excitons can generally be understood in the solid state language as localization of electronic (and hole) states.

Vibrational excitons on the other hand are often defined in the opposite direction. They occur in systems with identical localized vibrational chromophores. Resonant interaction between these localized vibrations then leads to a delocalization of the vibrational wave function. Incidentally, these exciton states can be described by the same theory used to describe Frenkel excitons [8], which is the main reason for using the same term for this physically quite different excitation. However, in principle vibrational excitons can also be understood as localized phonons, where the localization is due to structural disorder that can happen on various length scales.

The smallest vibrational excitons are found in molecular dimers, where the coupling between two degenerate vibrational modes leads to the so-called Davydov splitting of the vibrational transition frequencies [41], a phenomenon frequently encountered in molecular crystals [102]. The new vibrational eigenstates are often symmetric and antisymmetric, respectively. In some way, even the symmetric/antisymmetric splitting of the stretching vibrations in water and formamide can be understood as formation of, in this case intramolecular, exciton states. Most commonly, vibrational excitons are discussed in proteins and polypeptides where the strongly interacting amide I and II modes form largely delocalized states whose properties are indicative of the polypeptide structure and pro-
tein secondary and tertiary structure [14, 81, 84–99]. But also geometrical constraints such as for nanostructures and structural disorder can lead to localization of phonon modes, i.e. formation of vibrational excitons [103, 104].

All these systems however, exhibit essentially static structures. The treatment of the excitonic nature of vibrational excitations in this case relies on an eigenstate analysis, which is referred to as the exciton basis [8]. Small amplitude fluctuations, for example solvent interactions in proteins, can be treated in a statistical manner. Nonetheless, this description relies on structural stability such that the nature of the excitonic states is conserved, at least on short time scales. It is this assumption that does not hold for vibrational excitons in liquids.

Little is known about vibrational excitons in neat liquids at the moment. Experimental evidence of the existence of delocalized vibrational excitations in liquids was, up until this work, limited to the so-called Raman non-coincidence effect [60, 61, 83, 105–110]. In this polarized Raman experiment, a spectral difference between the peak positions of the isotropic and the anisotropic Raman signal is observed. It was shown that the effect arises from resonant vibrational coupling and is highly sensitive to medium range structural order, i.e. relative arrangement of the molecules [108]. The extent of delocalization defining the size of the structural domain mapped by the excitons is a result of competition between local disorder and resonant coupling strength [111]. These experiments and simulations are however linear, i.e. sensitive only to average liquid structure and the harmonic part of the intermolecular potential. It is the central theme of this work to show how ultrafast vibrational spectroscopy of such vibrational excitons in neat liquids allows access to structural dynamics on intermediate length scales.
Chapter 3

Ultrafast Vibrational Spectroscopy

This chapter lays out the principles of ultrafast vibrational spectroscopy, largely focussing on third order spectroscopic techniques. It draws from the Ph.D theses of Nils Huse [41] and Darren Kraemer [46], as well as Shaul Mukamel’s book [7]. The concepts and problems presented here provide an important background for all experimental and theoretical studies performed in this work.

3.1 Nonlinear Optical Response

If electric fields $E(R, t)$ interact with a medium, they can induce a transient polarization $P(R, t)$. Following Maxwell’s equations, this induced polarization acts as a source term for emission of an electric field $E_{em}(R, t)$. In the linear response limit, this emitted electric field is due to interactions of the incoming field and the material response, resulting in linear absorption and dispersion, usually described by a complex valued refractive index. The frequency dependency of the complex refractive index is characteristic of a given medium, allowing access to information on the quantum mechanical properties of the medium.

A general description of the polarization induced by external fields is often given in terms of the susceptibility $\chi(\omega)$ in the frequency domain. It is useful to expand the
polarization in terms of powers of the electric field,

\[
P_i(\omega) = \chi^{(1)}_{ij}(\omega)E_j(\omega) + \chi^{(2)}_{ijk}(\omega, \omega_1, \omega_2)E_j(\omega_1)E_k(\omega_2) + \chi^{(3)}_{ijkl}(\omega, \omega_1, \omega_2, \omega_3)E_j(\omega_1)E_k(\omega_2)E_l(\omega_3) + \ldots \tag{3.1}
\]

where \( P_i \) are the polarization components, \( E_j \) are the electric field components and \( \chi^{(n)} \) are the electric susceptibility tensors of order \( n + 1 \).

The susceptibility tensors are especially useful for parametric processes, that is for nonlinear interactions at frequencies far from molecular resonances. Common examples of such interactions are refraction and birefringence in the linear regime, frequency doubling, sum or difference frequency generation as second order or \( \chi^{(2)} \) processes, and frequency tripling as a \( \chi^{(3)} \) interaction.

If the nonlinear interactions involve molecular resonances, the induced nonlinear polarization is no longer instantaneous with respect to the incoming fields. It is then often more useful to describe the problem quantum mechanically and in the time domain using nonlinear optical response functions.

### 3.1.1 Optical Response Functions

In order to solve the quantum mechanical problem, a number of approximations are made. In a semiclassical approach, the molecular system is treated quantum mechanically and the external fields are treated classically. The interaction between the fields and the molecular system is described using the dipole approximation. Additionally, the low frequency motions (\( \hbar \omega \ll kT \)) are treated classically, leaving only the high frequency motions (\( \hbar \omega \gg kT \)) to be solved quantum mechanically. Then, the Hamiltonian can be written as:

\[
\hat{H}(t) = \hat{H}_0 - \hat{\mu} \cdot \mathbf{E}(\mathbf{R}, t) \tag{3.2}
\]
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Here,  \( \hat{H}_0 \) denotes the molecular Hamiltonian, \( \mathbf{E}(\mathbf{R}, t) \) is the (classical) external field interacting with the system via the quantum mechanical dipole operator \( \hat{\mu} \).

The induced polarization is defined as the expectation value of the dipole operator, which is most conveniently calculated in a density matrix formulation:

\[
P(t) = \langle \hat{\mu} \rho(t) \rangle
\]

where \( \rho(t) \) is the density matrix and \( \langle \rangle \) denotes the ensemble average, i.e. the trace over \( \hat{\mu} \rho \). Solving this problem means calculating the time dependence of the density matrix given by the Liouville-Von Neumann equation (\( \hbar = 1 \) throughout this work):

\[
\frac{\partial \rho(t)}{\partial t} = -i[\hat{H}(t), \rho(t)]
\]

This equation can be formally solved by integration plugging it into itself iteratively.

\[
\rho(t) = \rho(t_0) + \sum_{n=1}^{\infty} (-i)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \times [\hat{H}(\tau_n), [\hat{H}(\tau_{n-1}), \cdots [\hat{H}(\tau_1), \rho(t_0)] \cdots]]
\]

By switching to the interaction picture (denoted by index \( I \)), this expression can be rewritten in terms of powers \( n \) of the external electric fields analogously to the susceptibility expression Eq. 3.2.

\[
\rho_I(t) = \rho_I(t_0) + \sum_{n=1}^{\infty} i^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \mathbf{E}(\tau_1) \cdots \mathbf{E}(\tau_{n-1}) \times [\hat{\mu}_I(\tau_n), [\hat{\mu}_I(\tau_{n-1}), \cdots [\hat{\mu}_I(\tau_1), \rho(t_0)] \cdots]]
\]

where \( \hat{A}_I = \hat{G}_I \hat{A} \hat{G}_I^\dagger \), \( \rho_I = \hat{U}^\dagger \rho \hat{U} \) with the time evolution operator \( G(t_1, t_0) = \exp(-i\hat{H}_0(t_1-
often referred to as Greens function. For simplicity, the dipole operator in the interaction picture will in the following be denoted as \( \hat{\mu}(t) \) only, since it is time independent in the Schrödinger picture. Because the trace in Eq. 3.3 is independent of the chosen representation, the induced polarization can now be calculated for each order \( n \) of the interaction. This separation into different orders of response allows the perturbative approach to the nonlinear response.

\[
P^{(n)}(t) = i^n \int_{-\infty}^{t} d\tau_n \int_{-\infty}^{\tau_n} d\tau_{n-1} \ldots \int_{-\infty}^{\tau_2} d\tau_1 E(\tau_n) E(\tau_{n-1}) \ldots E(\tau_1) \\
\times \langle \hat{\mu}(t)[\hat{\mu}(\tau_n), [\hat{\mu}(\tau_{n-1}), \ldots [\hat{\mu}(\tau_1), \rho(-\infty)] \ldots]\rangle \tag{3.7}
\]

Eq. 3.7 is used to define the \( n \)'th order nonlinear response functions \( S^{(n)} \) in the time domain, \( t_k = \tau_{k+1} - \tau_k \):

\[
P^{(n)}(t) = \int_{-\infty}^{\infty} dt_n \ldots \int_{-\infty}^{\infty} dt_1 E(t - t_n - \ldots - t_1) \ldots E(t - t_n) \\
\times S^{(n)}(t_1, \ldots, t_n) \\
S^{(n)}(t_1, \ldots, t_n) = i^n \theta(t_n) \ldots \theta(t_{n-1}) \theta(t_n) \\
\times \langle \hat{\mu}(\tau_{n+1})[\hat{\mu}(\tau_n), \ldots [\hat{\mu}(\tau_1), \rho(-\infty)] \ldots]\rangle \tag{3.8}
\]

where the Heaviside functions \( \theta(t_k) \) conserve the causality. As seen in Eq. 3.8, the \( n \)'th order response involves \( n + 1 \) dipole interactions; \( n \) originating from the external fields and one emitting the nonlinear polarization. The most relevant response functions for this work are the first order or linear response function \( S^{(1)} \) and the third order response
function $S^{(3)}$, again $t_k = \tau_{k+1} - \tau_k$:

$$S^{(1)}(t_1) = i\theta(t_1)\langle \hat{\mu}(\tau_2)\hat{\mu}(\tau_1), \rho(-\infty) \rangle$$
$$S^{(3)}(t_1, t_2, t_3) = -i\theta(t_1)\theta(t_2)\theta(t_3)\langle \hat{\mu}(\tau_4)\left[\hat{\mu}(\tau_3), \left[\hat{\mu}(\tau_2), \left[\hat{\mu}(\tau_1), \rho(-\infty)\right]\right]\right]\rangle$$

In the commonly used impulsive limit, i.e. assuming extremely short and well separated pulses, the field interactions in Eq. 3.8 are assumed to be $\delta$-functions. Then, the nonlinear polarization is simply proportional to the respective response function. For finite pulse durations, the convolution integrals in Eq. 3.8 have to be carried out explicitly.

### 3.1.2 Double Sided Feynman Diagrams

Since the double sided Feynman diagrams are an essential tool throughout this work, they are derived and explained in quite some detail here.

After writing out the commutators in Eq. 3.9, the different terms can then be interpreted as different Liouville pathways accessible in the given order of response. A common way of depicting such pathways is using Feynman diagrams. In that sense, the total response is given by summing up all possible pathways or diagrams, a standard approach in quantum mechanics. It is instructive to first examine the linear response function.

$$S^{(1)}(t_1) = i\theta(t_1)\left(\langle \hat{\mu}(\tau_2)\hat{\mu}(\tau_1)\rho(-\infty) \rangle - \langle \hat{\mu}(\tau_2)\rho(-\infty)\hat{\mu}(\tau_1) \rangle\right)$$

The next step is to apply the rotating wave approximation. In the given context, this means assuming the dipole operator to always transfer the density matrix between a population state ($|0\rangle\langle 0|, |1\rangle\langle 1|, \ldots$) and a coherence state ($|1\rangle\langle 0|, |0\rangle\langle 1|, |1\rangle\langle 2|, \ldots$) or
vice versa. Then, the dipole operator can be rewritten consisting of two terms, in the harmonic limit:

$$\hat{\mu} = \hat{\mu}^+ + \hat{\mu}^- = \mu \hat{B}^\dagger + \mu \hat{B}$$  \hspace{1cm} (3.11)$$

where $\mu$ is the (classical) transition dipole moment and $\hat{B}^\dagger (\hat{B})$ are the harmonic creation (annihilation) operators with $[\hat{B}^\dagger_i, \hat{B}_j] = \delta_{ij}$. The modes of interest are high frequency, i.e. $\hbar \omega \gg kT$, which means that the initial density matrix can safely be assumed to be in ground state $|0\rangle \langle 0|$. Then, plugging Eq. 3.11 into Eq. 3.10 causes 6 of the total 8 terms to vanish, leaving:

$$S^{(1)}(t_1) = i\theta(t_1)\left(\langle \hat{\mu}^-(\tau_2)\hat{\mu}^+(\tau_1)\rho(-\infty)\rangle - \langle \hat{\mu}^+(\tau_2)^+\rho(-\infty)\hat{\mu}^-(\tau_1)\rangle \right)$$

$$= i\theta(t_1)\left(\langle \hat{\mu}^-(\tau_2)\hat{\mu}^+(\tau_1)\rho(-\infty)\rangle - \langle \rho(-\infty)\hat{\mu}^-(\tau_1)\hat{\mu}^+(\tau_2)\rangle \right)$$

$$= i\theta(t_1)\left(\langle \hat{\mu}^-\hat{\mu}^+\rangle - \langle \rho(\tau_1)\rho(\tau_2)\rangle \right)$$  \hspace{1cm} (3.12)$$

In the second line of Eq. 3.12, cyclic permutation within the trace was used to rearrange the interactions in a more intuitive way. In the first term, $\hat{\mu}^+$ creates a $|1\rangle \langle 0|$ coherence at time 0, which is then destroyed again at time $t$ with $\hat{\mu}^-$. In the second term, the situation is identical, only here the creation happens from the right side of the density matrix leading to a $|0\rangle \langle 1|$ coherence. It is now obvious that these two diagrams are simply complex conjugates of each other, resulting in a real valued expectation value of the total polarization operator. As a consequence, in general only half the diagrams have to be evaluated. Nonetheless, the full Eq. 3.12 is very useful for introducing the double sided Feynman diagrams, which are shown in Fig. 3.1.

Since the theory is developed in a density matrix formalism (or in Liouville space), the Feynman diagrams are double sided to represent the ket and the bra side of the
Figure 3.1: Double sided Feynman diagrams for the linear response. The diagrams correspond to the two terms in Eq. 3.12. On the left, the first dipole excites a coherence from the left side of the diagram (creation with $\hat{\mu}^+$ at time 0), which is destroyed at time $t$. On the right side, the creation happens from the right side of the density matrix with the conjugate operator. The two diagrams are complex conjugates of each other.

density matrix. The vertical axis is time, starting at time $\tau_1$ at the bottom. The solid vertical lines stand for the evolution of the ket and the bra side of the density matrix. Each arrow represents a dipole interaction. Incoming arrows create excitations by increasing the quantum number of a bra or a ket by one, outgoing ones destroy or deexcite, reducing a quantum number by one. This corresponds to $\hat{\mu}^+ (\hat{\mu}^-)$ and $\hat{\mu}^- (\hat{\mu}^+)$ on the left (right) side of the diagrams, respectively. The last (latest) interaction is always outgoing, representing the emission of the induced polarization.镜射一个图象关于垂直轴得到的是其共轭图象。 Additionally, the direction of the arrows are indicative of a given phase matching condition, which will be discussed in more detail below. In short, when assigning a wave vector $\mathbf{k}$ to each dipole interaction, arrows pointing right will have a positive $\mathbf{k}$, while arrows pointing left have a negative value, $-\mathbf{k}$. The phase matching for a given diagram is given by the sum of all wave vectors being zero, which defines the direction of the emitted field $\mathbf{k}_S = \sum_k \mathbf{k}_j$ for the $n$'th order response.

Even though the induced linear or nonlinear polarization is real-valued, the signal electric field emitted by this polarization is usually considered to be complex, i.e. also has a phase. This can be understood in the linear response as the phase difference between the signal field and the incoming field. This phase difference determines whether the given interaction is dispersive (phase change of the incoming field) or absorptive (amplitude
change of the incoming field). Most conveniently, this information is already contained in the complex valued response functions (only considering half the diagrams), where the real and imaginary components of the response functions correspond to the dispersive and absorptive contributions to the signal, respectively.
Figure 3.2: Double sided Feynman diagrams for the third order vibrational response. Signals along three possible phase matching conditions $k_I$, $k_{II}$, $k_{III}$ are shown, usually referred to as rephasing, non-rephasing and double quantum coherence pathways, respectively. $S_{1,4}$ are called ground state bleach because of the ground state population during $t_2$ evolution. Similarly, $S_{2,5}$ are referred to as induced emission from the excited state and $S_{3,6}$ are called excited state absorption diagrams.

### 3.1.3 Third Order Response

Following these ideas, the commutators in the third order response function Eq. 3.9 can be expanded. The three nested commutators create a total of 8 terms:
\[ S^{(3)} = -i \theta(t_1) \theta(t_2) \theta(t_3) \left( \right. \\
+ \langle \hat{\mu}(\tau_4) \hat{\mu}(\tau_3) \hat{\mu}(\tau_2) \hat{\mu}(\tau_1) \rho(-\infty) \rangle \\
- \langle \hat{\mu}(\tau_4) \hat{\mu}(\tau_3) \rho(-\infty) \hat{\mu}(\tau_1) \rangle \\
\sum_{k=1}^{IV} (R_k - R_k^*) \left. \right) \] (3.13)

giving a total of four relevant contributions \( R_k \) and their complex conjugates \( R_k^* \) to the third order response:

\[ R_I = \langle \hat{\mu}(\tau_4) \hat{\mu}(\tau_3) \hat{\mu}(\tau_2) \hat{\mu}(\tau_1) \rho(-\infty) \rangle \]
\[ R_{II} = \langle \hat{\mu}(\tau_4) \hat{\mu}(\tau_3) \rho(-\infty) \hat{\mu}(\tau_1) \hat{\mu}(\tau_2) \rangle \]
\[ R_{III} = \langle \hat{\mu}(\tau_4) \hat{\mu}(\tau_2) \rho(-\infty) \hat{\mu}(\tau_1) \hat{\mu}(\tau_3) \rangle \]
\[ R_{IV} = \langle \hat{\mu}(\tau_4) \hat{\mu}(\tau_1) \rho(-\infty) \hat{\mu}(\tau_2) \hat{\mu}(\tau_3) \rangle \] (3.14)

For an isolated two-level system, these four contributions can directly be translated into four double sided Feynman diagrams. For multi-level systems like molecular vibrations or a system of coupled two-level modes, the situations is slightly more complex, since a dipole acting on a first excited ket or bra can either deexcite to the ground state, or excite further up into the 2nd excited state. Therefore, the above four contributions then result in a total of 8 independent Liouville pathways \( S_{1-8} \) (and their respective complex conjugates) given in Eq. 3.15 and depicted as double sided Feynman diagrams in Fig. 3.2.
\[
S_1 = \langle \hat{\mu}^-(\tau_4)\hat{\mu}^+(\tau_3)\rho(-\infty)\hat{\mu}^-(\tau_1)\hat{\mu}^+(\tau_2) \rangle \\
S_2 = \langle \hat{\mu}^-(\tau_4)\hat{\mu}^+(\tau_2)\rho(-\infty)\hat{\mu}^-(\tau_1)\hat{\mu}^+(\tau_3) \rangle \\
S_3 = -\langle \hat{\mu}^-(\tau_4)\hat{\mu}^+(\tau_3)\rho(-\infty)\hat{\mu}^+(\tau_1)\hat{\mu}^-(\tau_2) \rangle \\
S_4 = \langle \hat{\mu}^-(\tau_4)\hat{\mu}^+(\tau_3)\hat{\mu}^-(\tau_2)\rho(-\infty)\hat{\mu}^+(\tau_1) \rangle \\
S_5 = \langle \hat{\mu}^-(\tau_4)\rho(-\infty)\hat{\mu}^+(\tau_1)\hat{\mu}^+(\tau_2)\hat{\mu}^-(\tau_3) \rangle \\
S_6 = -\langle \hat{\mu}^-(\tau_4)\hat{\mu}^+(\tau_3)\hat{\mu}^+(\tau_1)\rho(-\infty)\hat{\mu}^+(\tau_2) \rangle \\
S_7 = \langle \hat{\mu}^-(\tau_4)\hat{\mu}^+(\tau_3)\hat{\mu}^+(\tau_2)\hat{\mu}^+(\tau_1)\rho(-\infty) \rangle \\
S_8 = -\langle \hat{\mu}^-(\tau_4)\hat{\mu}^+(\tau_2)\hat{\mu}^+(\tau_1)\rho(-\infty)\hat{\mu}^+(\tau_3) \rangle \
\] (3.15)

By convention, the diagrams with \( k_S \) pointing left are depicted, their complex conjugates are the mirrored diagrams with \( k_S \) pointing right. These 8 pathways can be sorted according to their phase matching condition. Diagrams \( S_{1-3} \) have \( k_S = -k_1 + k_2 + k_3 \equiv k_I \) and are referred to as rephasing pathways. Diagrams \( S_{4-6} \) with \( k_S = k_1 - k_2 + k_3 \equiv k_I\) are called non-rephasing pathways. The terms rephasing and non-rephasing relate to the capability of the given diagrams to generate an echo signal as will be discussed below in Sec. 3.2.4. In some cases also the so-called double quantum coherence pathways \( S_{7,8} \) with \( k_S = k_1 + k_2 - k_3 \equiv k_{II} \) are considered. The total response for each phase matching condition is given by the sum of all respective diagrams:

\[
S_I = S_1 + S_2 + S_3 \\
S_{II} = S_4 + S_5 + S_6 \\
S_{III} = S_7 + S_8 \
\] (3.16)

Since the more commonly used diagrams \( S_{1-6} \) show a population state of the density
matrix \(|n\rangle\langle n|\) during \(t_2\), this evolution time is often called the population time. The diagrams \(S_1\) and \(S_4\) are referred to as ground state bleach (GSB) diagrams, because they involve a ground state population \(|0\rangle\langle 0|\) during \(t_2\). Similarly, \(S_{2,5}\) show a population in the first excited state \(|1\rangle\langle 1|\) during \(t_2\), with the third interaction deexciting back to a ground state coherence \(|1\rangle\langle 0|\), hence the name excited state emission (ESE). Finally for diagrams \(S_{3,6}\), the third interaction excites into a coherence between first and second excited state and is therefore referred to as excited state absorption (ESA).

In ultrafast spectroscopy, each dipole interaction is applied with an ultrashort laser pulse. This allows to scan the times \(t_1, t_2, t_3\) by changing the delays between the pulses in order to fully map the third order response of the system directly in the time domain. The geometric arrangement of the beams can additionally select a certain phase matching geometry.

### 3.1.4 The Echo

As discussed above, the \(k_I\) phase matching condition contains the *rephasing* pathways, since they are capable of producing a photon echo and as such, separate the homogeneous and inhomogeneous contributions to the third order signal. On the other hand, the \(k_{II}\) phase matching diagrams are called *non-rephasing*, since no photon echo is generated.

The overall third order polarization of a molecular system is an ensemble average measurement and it decays as a function of its evolution time \(t\). For the \(k_{II}\) pathways, the microscopic origin of this decay is, in a simplified description, a convolution of two major processes:

1. inhomogeneous dephasing: If the ensemble has a distribution of frequencies, the nonlinear polarization will oscillate with the average frequency. But with increasing \(t\), the individual oscillators get more and more out of phase due to their different frequencies. This leads to partial, and eventually full cancellation of the different contributions and a vanishing macroscopic polarization. The decay time of the
polarization can directly be related to the width of the inhomogeneous frequency
distribution.

2. homogeneous dephasing: Each oscillator in the ensemble experiences fluctuations of
the environment leading to fluctuating transition frequencies. If these fluctuations
are random, each oscillator experiences different modulations and their oscillations
will get out of phase and start cancelling each other. This leads to decay of the
overall polarization.

It is clear, that only the homogeneous contributions to the decay of the polarizations
can actually be related to structural dynamics, whereas inhomogeneous dephasing is
present even for a static structure. For that reason, the $k_{II}$ signal is often called free
induction decay.

The $k_I$ or photon echo signal on the other hand removes the inhomogeneous contri-
bution to the polarization decay. This can be understood by closely studying the double
sided Feynman diagrams in Fig. 3.2, focussing on the GSB diagrams $S_1$ and $S_4$. One way
of interpreting these diagrams is to see them as a measure of correlation between the two
coherences during $t_1$ and $t_3$. In that sense, the difference between these two diagrams is
the phase factor of the coherence during $t_1$, i.e. $|1\rangle \langle 0|$ vs. $|0\rangle \langle 1|$. This can be interpreted
as these two coherences propagating in the opposite direction in phase space.

In $S_4$ the coherences during $t_1$ and $t_3$ have the same phase factor. This means that any
inhomogeneous dephasing accumulated during $t_1$ is further propagated during $t_3$. In $S_1$
on the other hand, the $t_1$ and $t_3$ propagations are opposite, meaning that inhomogeneous
dephasing during $t_1$ is reversed during $t_3$. As a consequence, the signal will increase as
a function of $t_3$ since the oscillators get back in phase to peak at $t_3 = t_1$. This exact
peaking of the signal response is called the echo or rephasing. The appearance of the
echo shows that the individual frequency fluctuations have not yet destroyed the local
coherences. Instead, the decay of the amplitude of the echo signal is directly related to
the homogeneous dephasing component only. The photon echo signal therefore separates
the homogeneous and inhomogeneous contributions to the signal decay.

The idea of cancelling the inhomogeneous dephasing by observation of the echo originated from 2D NMR spectroscopy \([30]\). However, here the interactions are in the strong-field limit, where the flipping of the propagation direction of the coherences is achieved with a given pulse area, as opposed to the phase matching conditions of the weak field interactions facilitated in nonlinear laser spectroscopy.

### 3.2 Third Order Infrared Spectroscopies

In principle, all third order spectroscopic techniques probe the same contributions to the nonlinear response of the molecular system under study. However, using various geometric arrangements (phase matching), pulse sequences and detection methods, most techniques only access parts of the nonlinear response and are by design sensitive to different microscopic processes.

The most commonly used third order method - pump probe spectroscopy (PPS) - is sensitive mainly to population dynamics, i.e. population relaxation and transfer dynamics. In contrast, all photon echo spectroscopies are, in principle, coherent techniques sensitive to dynamics of the coherences. The various photon echo techniques however, again differ significantly in the microscopic information accessible. As such, heterodyne transient grating measures population dynamics equivalent to PPS, homodyne two-pulse photon echo (2PE) can assess overall dephasing dynamics, and homodyne three pulse echo (3PE) can access different time scales of spectral diffusion. The most general technique is heterodyne three pulse echo, which is usually evaluated in the frequency domain as two-dimensional spectra, and gives access to the full third order response of the system.
3.2.1 Homodyne vs. Heterodyne Detection

As a result of the phase matching conditions, the induced nonlinear polarization can emit the nonlinear signal into a direction spatially isolated from the excitation beams. This has the great advantage that the signal is intrinsically background free. Detection of the optical signal is however, apart from recent advances in terahertz spectroscopy [76], limited to measuring the time-integrated intensity \( I_S \) of the complex signal fields in the given phase matching direction:

\[
I_S = \int_0^\infty dt |P^{(3)}(t)|^2 = |E_S|^2
\]  

(3.17)

Such direct detection of a nonlinear signal is called homodyne detection. Even though the background free character of the measurement usually improves the signal-to-noise ratio (SNR) of the detection, the signals still tend to be very weak. As a result, the detector noise limited SNR is often small. Additionally the phase information within the signal field is lost in the quadratic nature of the measurement.

These problems can be avoided by interfering the nonlinear signal field with a strong known electric field called the local oscillator (LO), \( E_{LO} \), in a process known as heterodyne detection:

\[
I = |E_{LO} + E_S|^2 = |E_{LO}|^2 + |E_S|^2 + 2E_{LO}E_S \cos(\phi_{LO} - \phi_S)
\]  

(3.18)

where \( \phi_{LO} - \phi_S \) is the absolute phase difference between the two fields. Since \( |E_{LO}| \gg |E_S| \), the heterodyne detected intensity basically consists of a constant term (\( |E_{LO}|^2 \)) and the interference term \( 2E_{LO}E_S \cos(\phi_{LO} - \phi_S) \), which is the main observable. This signal is amplified (by a factor \( |E_{LO}|/|E_S| \)) compared to the homodyne signal and linearized. Additionally, the full complex electric field of the nonlinear signal is accessible by scanning the absolute phase difference between the two fields.

However, heterodyne detection is experimentally much more challenging, since it is
an interferometric measurement that requires rigorous phase stabilization between the optical beams.

### 3.2.2 Pump Probe Spectroscopy

In pump probe spectroscopy, the 3rd order response is induced by two short laser pulses: a strong pump pulse $E_{\text{pump}}$ and a weak probe pulse $E_{\text{probe}}$. The pump pulse is assumed to be responsible for the first two dipole interactions with the sample, creating a population state, while the weak probe is delayed and creates the coherence in the sample that then irradiates the nonlinear signal. By having a slight angle between the two beams when focused onto the sample, the phase matching conditions select the diagrams $S_{1-6}$ to emit the nonlinear signal collinear with the probe beam. The delay between the two pulses corresponds to the population time $t_2$. A schematic representation of the pump probe technique is shown in Fig. 3.3.

![Figure 3.3: Schematic of the pump probe technique. With a slight angle between the pump and the delayed probe beams, the nonlinear signal emitted in the probe direction is interfered with the probe beam on the detector.](image)

Since the 3rd order signal is collinear with the probe beam, the experiment is *self heterodyned* with the probe acting as the local oscillator. Intrinsically, the absolute phase difference between the probe and the signal field is fixed to zero. As a result, pump probe spectroscopy can only detect the real or absorptive component of the 3rd order response, corresponding to a transmission change $\Delta T$ of the probe field. If spectrally dispersed for
weak signals,

\[
\Delta T(t_2, \omega) = \frac{I(t_2, \omega)}{I_0(\omega)} = \frac{\int dt |E_{\text{probe}}(\omega)|^2 + |E_{\text{signal}}(\omega, t_2)|^2}{\int dt |E_{\text{probe}}(\omega)|^2} 
\approx 1 + 2 \frac{\int dt \Re(E_{\text{probe}}(\omega) E_{\text{signal}}^*(\omega, t_2))}{\int dt |E_{\text{probe}}(\omega)|^2}
\]

(3.19)

Here, \( I \) and \( I_0 \) denote the probe intensity with and without the pump pulse, achieved by chopping the pump beam. \( \int dt \) describes the temporal integration performed by the detector. As an intrinsic advantage of heterodyne detected signals, the transmission change can be negative or positive, corresponding to bleaching and increased absorption, respectively.

For positive population times in the impulsive limit, a simplified version of the Liouville pathways contributing to the transmission change can be derived, as shown in Fig. 3.4. Since the first two interactions originate from the pump pulse, the first delay time \( t_1 \) (coherence time) can be assumed to be zero. Then, the rephasing and non-rephasing pathways are identical. This is one way of identifying pump probe spectroscopy as an incoherent technique since it's not sensitive to the coherence evolutions. Instead, it mostly monitors the dynamics of the population states \(|n\rangle\langle n|\) during population time \( t_2 \).

For negative delay times (probe pulse preceding the pump pulse) the situation is quite different, and can be understood as a change in time ordering in the Feynman diagrams. The probe pulse then acts first (\( k_1 \)) and the two pump interactions transfer the \( t_1 \) coherence into the \( t_3 \) coherence, no persisting populations are created. Due to the geometry, only the non-rephasing pathways \( S_{4-6} \) contribute to the signal, which occurs as a time-inverted free induction decay. Additional coherent contributions to the pump probe signal appear during pulse overlap (small \( t_2 \) times), originating from multiple nonlinear processes and are generally referred to as \textit{coherent artifact}, the most prominent contribution being the so-called \textit{cross-phase modulation}. 
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Figure 3.4: Double sided Feynman diagrams contributing to the transmission change measured with pump probe spectroscopy. In the impulsive limit and the pump pulse preceding the probe pulse, the coherence time $t_1$ can be set to 0 and the rephasing and non-rephasing diagrams are pairwise identical.

The major strength of pump probe spectroscopy lies in monitoring population dynamics that can be grouped into two categories: population transfer and population relaxation. The former resonantly transfers energy between different modes in the same frequency range, the latter couples the excited high frequency modes to intramolecular or intermolecular lower frequency modes - the first step in the relaxation and, eventually, thermalization process of the deposited vibrational energy. In principle, the physics of both processes are identical. The distinction is rather based on whether the given process can be considered a relaxation process, i.e. relaxing the system in an energetically more favorable state.

Population transfer can be observed mainly in two ways: (a) between two spectrally distinct species, monitoring the spectrally resolved transmission dynamics (b) between modes with different orientations of their transition dipoles interacting with the excitation fields. This is achieved by using polarized excitation beams.

3.2.3 Magic Angle and Polarization Anisotropy

The decay of a pump probe bleaching or excited state absorption signal can be caused by (a) relaxation of the pump induced population state and/or (b) orientational relaxation
of the excited transition dipoles, either by rotational motion of the molecules in the liquid or by energy transfer to modes with different orientation. The latter (b) is caused by the vectorial character of the transition dipole moments and external electric fields.

The most common approach to distinguish true population dynamics from rotational relaxation is to apply polarized excitation beams. A rotation-free signal is acquired using the so-called Magic Angle (MA) arrangement, where the angle between the pump and the probe polarization is set to $\theta_{\text{MA}} = 54.7^\circ$. This angle is simply a result of the statistics of an ensemble of randomly oriented transition dipoles. Alternative to setting this specific angle, it is also possible to measure two signals, with parallel ($\parallel$) and perpendicular ($\perp$) polarization of the pump and probe beams. The rotation-free pump probe signal $\Delta T_{\text{MA}}$ is then given by:

$$\Delta T_{\text{MA}}(\omega, t_2) \propto \Delta T_{\parallel}(\omega, t_2) + 2\Delta T_{\perp}(\omega, t_2)$$  \hspace{1cm} (3.20)

Following the same idea, the rotational dynamics can be isolated by measuring the Polarization Anisotropy (PA) dynamics, here denoted as $r(\omega, t_2)$:

$$r(\omega, t_2) = \frac{\Delta T_{\parallel}(\omega, t_2) - \Delta T_{\perp}(\omega, t_2)}{\Delta T_{\parallel}(\omega, t_2) + 2\Delta T_{\perp}(\omega, t_2)}$$  \hspace{1cm} (3.21)

This signal is unaffected by population relaxation and only measures orientational dynamics, caused either by rotational relaxation or energy transfer. For isotropic media and linear transition dipole moments, the initial value of the polarization anisotropy is always $r(0) = 0.4$.

The idea of using polarized excitation beams to isolate orientational and relaxation dynamics can also be applied to other third order techniques, such as photon echo spectroscopy. The analogous expression for MA and PA signals can be derived.
3.2.4 Photon Echo Spectroscopy

All photon echo techniques separate the first two interactions $k_1$ and $k_2$, which are applied with two distinct ultra short laser pulses in contrast to the one strong pump pulse in PPS. This allows one to monitor the coherence dynamics by scanning the delay between these two pulses, in the impulsive limit, corresponding to the coherence time $t_1$ in Fig. 3.2. Three important photon echo techniques are commonly used, as shown schematically in Fig. 3.5.

Homodyne detected 2PE, Fig. 3.5 (a), measures the intensity of the nonlinear signal field as a function of the delay between the first pulse and a second, stronger pulse acting as dipole interactions two and three. In the impulsive limit, the nonlinear signal is proportional to the response function. The delay time then corresponds to the coherence time $t_1$ in the Feynman diagrams in Fig. 3.2. The signal along the $k_I$ phase matching condition is usually acquired spectrally integrated. Using Eq. 3.16, it can be written as:

$$S_{2PE}(t_1) \propto \int_0^{\infty} dt_3 |S_\ell(t_3, 0, t_1)|^2$$

(3.22)

The signal as a function of $t_2$ displays the overall dephasing dynamics and, for samples with inhomogeneous contributions to the dephasing, will show a maximum for $t_2 > 0$. This peak shift can be related to the degree of initial inhomogeneity of the transition frequencies in the ensemble. Even though the combination of the peak shift and the decay of the signal allows some insight into the dephasing mechanism, the information is highly convoluted. If the pulse order is reversed, the response is described by the double quantum coherence pathways $S_{7,8}$ which decay very rapidly, in most cases with a time constant well below the resolution of the experiment. As a consequence, the response is observed to rise instantaneously (within the time resolution). The signal along $k_{II}$ propagates collinearly with $k_1$, corresponding to a time-inverted pump-probe geometry.
Figure 3.5: Schematic representation of different photon echo techniques. (a) Homodyne detected two-pulse photon echo. (b) Homodyne detected three-pulse echo. (c) Heterodyne detected three pulse echo. The three excitation pulses are noncollinear, creating third order signals in distinct phase matching directions $k_I$ and $k_{II}$. Heterodyne detection in (c) is achieved with an additional pulse collinear with the signal beam.

Homodyne detected 3PE, Fig. 3.5 (b), additionally separates pulses two and three, both in time and direction. This allows scanning the population time $t_2$, as well as observing the signals along both the rephasing and non-rephasing pathways. In the impulsive limit, the signal along the $k_I$ phase matching condition is given by:
\begin{equation}
\begin{split}
S_{3PE,k_I}(t_1,t_2) \propto \int_0^\infty dt_3 (|S_I(t_3,t_2,t_1)|^2 + |S_{II}(t_3,t_2,-t_1)|^2)
\end{split}
\tag{3.23}
\end{equation}

The signal is now defined for positive and negative coherence times \( t_1 \), where negative \( t_1 \) values correspond to switching the time order of pulses one and two, i.e. switching from the rephasing \((S_{1-3})\) to the non-rephasing pathways \((S_{4-6})\). Due to symmetry reasons, the signal along \( k_{II} \) is identical to the signal along \( k_I \) with the coherence time axis inverted:

\begin{equation}
S_{3PE,k_I}(t_1,t_2) = S_{2PE,k_{II}}(-t_1,t_2)
\tag{3.24}
\end{equation}

The most important observable in 3PE experiments is the position of the maximum signal along \( t_1 \) as a function of \( t_2 \), usually referred to as the Photon Echo Peak Shift (PEPS). As mentioned earlier, the peak shift to positive values of \( t_1 \) can be related to the inhomogeneity of the transition frequencies. With increasing \( t_2 \), this peak shift decays due to frequency fluctuations, i.e. loss of inhomogeneity, and eventually approaches zero. The dynamics of the peak shift decay are related to the time scales of transition frequency fluctuations in the sample, generally referred to as spectral diffusion. The most prominent measure of spectral diffusion is the frequency correlation function (FCF) \( C(t) \):

\begin{equation}
C(t) = \langle \delta \omega(t) \delta \omega(0) \rangle
\tag{3.25}
\end{equation}

Apart from early times \( t_2 \), the PEPS signal directly resembles the FCF and is therefore a good and fairly direct measure of structural dynamics in the sample. Often, the \( k_I \) and \( k_{II} \) signals are measured simultaneously in order to remove the uncertainty of the \( t_1 = 0 \) position as a major error source to the PEPS values. Then, the PEPS is measured as half the \( t_1 \) distance between the \( k_I \) and \( k_{II} \) signal maxima.
The drawback of this method is twofold. On the one hand, the homodyne detected signals are weak and SNR tends to be a problem. On the other hand, the PEPS signal only reflects the ensemble averaged dynamics (see below for details, Sec. 3.3.2). It cannot distinguish between different species or distributions of species with different structural dynamics. Also, the 3PE experiments cannot access energy transfer or chemical exchange dynamics, simply due to the ensemble average nature of the measurement.

The full third order response information is accessible with heterodyne detected three pulse echo spectroscopy, see Fig. 3.5 (c). An additional weak LO pulse is introduced and interfered with the signal. Here, the LO pulse can either pass through sample as shown in the figure, or bypass the sample to be combined with the signal on the detector. Apart from scanning $t_1$ and $t_2$ with the respective delays, the $t_3$ dependence of the third order response can be acquired by either scanning the time delay of the LO pulse or by spectral interferometry, i.e. spectrally dispersing the signal field with a fixed delay of the LO pulse (see Sec. 4.3.1 for details). Most commonly, the heterodyne three pulse echo signal is analyzed in the frequency domain as two-dimensional spectra.

### 3.2.5 Two-Dimensional Coherent Spectroscopy

While the third order response function in the time domain contains all the information accessible by this order of spectroscopy, it is more useful and intuitive to switch to the frequency domain for the evolution of coherences during $t_1$ and $t_3$. This procedure is equivalent to Fourier Transform Infrared (FTIR) spectroscopy in the linear regime. The extension of this idea to the second frequency dimension originates from the equivalent NMR technique [30, 112]. The main advantage of the frequency domain analysis lies in the structure of the 2D spectra, that allows, to some extent, direct identification of microscopic processes governing the response from the peak positions and peak shapes in the 2D spectra.

Following the multiple connections to other techniques, a number of different names
The theoretical 2D spectrum in the impulsive limit is acquired from the time domain response expression by double Fourier transformation along the $t_1$ and $t_3$ coherence evolution times and is usually analyzed for selected values of the population time $t_2$.

$$S^{(3)}(\omega_1, t_2, \omega_3) = \int_0^\infty dt_1 \int_0^\infty dt_3 \exp(i(\omega_1 t_1 + \omega_3 t_3)) S^{(3)}(t_1, t_2, t_3)$$ (3.26)

In some cases, the rephasing and non-rephasing phase matching conditions are analyzed separately. But most commonly, the absorptive component of the third order response is plotted, which is acquired by scanning both negative and positive values of the coherence time $t_1$. For the response functions, negative values of $t_1$ correspond to switching the time order of $k_1$ and $k_2$, i.e. switching to the non-rephasing pathways, when measuring along the $k_I$ phase matching direction. Using Eq. 3.15, the third order response then is given by:

$$S^{(3)}_{k_I}(t_1, t_2, t_3) = S_I(t_1, t_2, t_3) + S_{II}(-t_1, t_2, t_3)$$ (3.27)

The absorptive component is given by the imaginary part of the double Fourier transformation of the response, $\Im(S^{(3)}_{k_I}(\omega_1, t_2\omega_3))$ (corresponding to the real part of the signal electric field).

A schematic, idealized series of 2D spectra for different population times $t_2$ is shown in Fig. 3.6 for illustration. By convention, the vertical axis $\omega_1$ represents the $t_1$ coherence, it is therefore called the excitation frequency axis. The horizontal axis is the detection axis, corresponding to the $t_3$ coherence. In general, the 2D spectra show correlations...
between excited and detected frequencies. Each point in the spectrum corresponds to the probability of detecting a signal at a given frequency \( \omega_3 \) if excited at \( \omega_1 \).

![Idealized 2D spectra for three two-level modes at different population times.](image)

**Figure 3.6**: Idealized 2D spectra for three two-level modes at different population times. Peak shapes elongated along the diagonal indicate the initial inhomogeneity of each species, that may decay as a function of \( t_2 \). With increasing \( t_2 \), cross peaks grow in due to energy transfer, indicated by the gray scale. The time \( t_c \) is taken to give the time scale of the overall dynamics. If the energy transfer maintains some of the inhomogeneity, the cross peaks appear tilted. The magnitude of the peaks is related to the overall population dynamics.

The idealized spectrum is composed of three spectrally distinct species A, B, and C. For clarity, all three modes are assumed to be two-level systems. At population time \( t_2 \), only peaks on the diagonal are observed. The peak shapes range from round for B, to slightly elongated along the diagonal for A and strongly elongated for C, indicative of the degree of inhomogeneity within each species sub-ensemble. With increasing \( t_2 \), the previously elongated diagonal peak shapes evolve to become uncorrelated, i.e. more round. This means that frequency fluctuations average out the inhomogeneous distributions within the sub-ensemble on the given \( t_2 \) time scales.

Additionally, cross peaks grow in as energy is exchanged between the different species. The magnitude and time scale of that growth is caused by the magnitude of coupling between the given pair of species. If some spectral inhomogeneity is maintained during the energy transfer process, the cross peaks can appear tilted. The peak volumes as a function
of $t_2$ can be related to the overall population dynamics, i.e. population transfer (volume of the cross peaks) and population relaxation (volume of the diagonal peaks and the cross peaks). Alternatively, the cross peaks can also be related to chemical exchange processes, where a chemical reaction structurally changes a molecule or compound resulting in a change of the spectral signature. In this case, the cross peak dynamics reflect the rates of the chemical reaction.

For vibrational modes, the 2D spectra display additional peaks due to excited state absorption processes ($S_3$ and $S_6$) which generally appear red shifted from the corresponding fundamental peak. The magnitude of that red shift directly reflects the anharmonicity of the vibrational mode, since it is given by the difference between the $0 \rightarrow 1$ and $1 \rightarrow 2$ energy gaps. This difference is called anharmonicity shift of the $1 \rightarrow 2$ transition and is 0 for harmonic systems.

For illustration, a series of simulated 2DIR spectra of a single vibrational chromophore subject to spectral diffusion is shown in Fig. 3.7 for different population times $t_2$. The simulation uses the Kubo model described in Sec. 3.3.2 with a spectral diffusion time scale of 200 fs. Each spectrum shows two peaks. The positive peak on the diagonal corresponds
to the fundamental $0 \rightarrow 1$ transition (GSB and ESE), the red shifted negative peak to the $1 \rightarrow 2$ ESA. The anti-diagonal peak width reports on the homogeneous contribution to the dephasing, the diagonal peak width represents the inhomogeneity, which decays as a function of $t_2$. If the anharmonicity shift is smaller or comparable to the antidiagonal peak width, the two peaks overlap and interfere in the overlap region, causing a distortion of the peak shapes.

These simple interpretations of the 2D spectra are based on extensive theoretical efforts. For more complex systems with respectively more complex dynamics, the peak shapes and magnitudes, and their evolution are often not as easily understood. However, the basic ideas and interpretations presented here are still a good starting point in most cases. In the following, some of the various theoretical approaches will be discussed, verifying such simple interpretations and extending the understanding to more complex situations.

### 3.3 Calculating the Nonlinear Response Functions

Connecting the third order response to certain microscopic processes requires understanding what signatures such processes produce in the response. This is usually achieved by setting up a model system that is capable of displaying these processes and then calculating the nonlinear response for that system. The most prominent processes accessible through third order spectroscopies are dephasing, spectral diffusion, energy transfer, chemical exchange, and population relaxation. By setting up the appropriate model systems, it is often possible to dissect the response to identify the major dynamic channels. The case of neat liquids however is often more complex. Here, all these processes are highly interconnected in a partially coherent manner, and the resulting dynamics need to be examined in a more general way.

However, before going into the details of response function calculations, it is useful
to review some essential quantum mechanical concepts.

### 3.3.1 Dephasing in Hilbert and Liouville Space

In the previous sections, the theoretical description of the nonlinear response has been described in Liouville space, i.e. as dynamics of the density matrix. The main reason for that approach lies in the physical observable common to all optical spectroscopies, that is, a polarization emitted by a molecular coherence. These molecular coherences are, by definition, a statistical property of an ensemble, and a native component of the Liouville space dynamics through the off-diagonal elements of the density matrix. A description in the wave function language associated with the Hilbert space seems counterintuitive.

This is most obvious when trying to include phenomenological relaxation terms. For a two-level system \{\ket{g}, \ket{e}\}, the Liouville-Von Neumann equation (Eq. 3.4) is a set of differential equations, the optical Bloch equations, that can be solved exactly. In the solution for small external fields and in the absence of dephasing, the diagonal elements of the density matrix are constant (populations) and the off-diagonal elements oscillate with the frequency corresponding to the energy gap between the two levels (coherences). Phenomenological relaxation can be introduced by adding a relaxation terms to Eq. 3.4:

\[
\frac{\partial \rho_{gg}(t)}{\partial t} = \frac{1}{T_1} \rho_{ee}(t) \\
\frac{\partial \rho_{ee}(t)}{\partial t} = -\frac{1}{T_1} \rho_{ee}(t) \\
\frac{\partial \rho_{eg}(t)}{\partial t} = -i \omega_{eg} \rho_{eg}(t) - \frac{1}{T_2^*} \rho_{eg}(t) \\
\frac{\partial \rho_{ge}(t)}{\partial t} = i \omega_{ge} \rho_{ge}(t) - \frac{1}{T_2^*} \rho_{ge}(t)
\] (3.28)

Here, \(T_1\) is the population relaxation time and \(T_2^*\) is the pure dephasing time of the coherences, and \(\omega_{eg}\) is the energy difference between the ground and the excited state.
The solution of this problem is of the form:

\[
\rho_{gg}(t) = 1 - \rho_{ee}(0) \exp \left(-t/T_1\right)
\]

\[
\rho_{ee}(t) = \rho_{ee}(0) \exp \left(-t/T_1\right)
\]

\[
\rho_{eg(ge)}(t) = \rho_{eg(ge)}(0) \exp \left(\mp i\omega_{eg} t\right) \exp \left(-t/T_2\right)
\]

with \[
\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*}
\]

Here, the dephasing time \(T_2\) was introduced as the decay constant of the coherence amplitudes, caused by both phase relaxation (pure dephasing, \(T_2^*\)) and population relaxation \((T_1)\).

When operating in Liouville space, the Liouville-Von Neumann equation (3.4) is often rewritten introducing the Liouville operator \(\hat{\mathcal{L}}\), defined through \(\hat{\mathcal{L}} \hat{A} = [\hat{H}, \hat{A}]\). The resulting equation is called the Liouville equation, and is the Liouville space equivalent of the Schrödinger equation in Hilbert space.

\[
\frac{\partial \rho}{\partial t} = -i\hat{\mathcal{L}}\rho
\]

Having this equivalency in mind, it is important to note that introducing phenomenological dephasing into the Schrödinger equation is ill-defined, just as the concept of the relaxation of a wave function is. Only in Liouville space it is possible to rewrite the phenomenological relaxation description Eq. 3.28 in a compact form with a single relaxation operator,

\[
\frac{\partial \rho}{\partial t} = -i\hat{\mathcal{L}}\rho - \hat{\Gamma} \rho
\]

where \(\hat{\Gamma}\) contains the respective relaxation constants.

Inspecting Eq. 3.30, the time evolution operator or Greens function \(\hat{G}\) introduced in
Hilbert space in Sec. 3.1.1, can be written in Liouville space.

\[
\hat{G}(t) = \theta(t) \exp(-i\hat{\mathcal{L}}t)
\]

\[\Rightarrow \rho(t + t_0) = \hat{G}(t)\rho(t_0) \tag{3.32}\]

If additionally the dipole interactions \(\hat{\mu}\) in Eq. 3.8 are replaced by the equivalent Liouville space operators \(\hat{V}\) [7], the first and third order response function expressions can be generally rewritten in the Liouville space language:

\[
S^{(1)}(t_1) = i \langle\langle \hat{V}\hat{G}(t_1)\hat{V}\rho(-\infty) \rangle\rangle
\]

\[
S^{(3)}(t_1, t_2, t_3) = -i \langle\langle \hat{V}\hat{G}(t_3)\hat{V}\hat{G}(t_2)\hat{V}\hat{G}(t_1)\hat{V}\rho(-\infty) \rangle\rangle \tag{3.33}\]

Here, \(\langle\langle \hat{A}\rho \rangle\rangle\) denotes the trace in Liouville space. Inspecting Eq. 3.33, the response function can be understood as a series of dipole interactions and propagations of the density matrix. Calculating the response will in most cases focus on calculating the Greens functions \(\hat{G}(t)\). Once the Greens functions are known, the response calculation is straightforward.

Alternatively, the response can also be evaluated in Hilbert space. The important concept here is the so-called closed time path loop introduced by S. Mukamel [7]. The idea is to treat the ket and the bra side of the density matrix separately as wave functions in Hilbert space. The diagrams can be evaluated going forward in time on the bra side of the diagram, and then backwards in time on the ket side. This is possible, because only diagrams ending in a true population state \(|n_i\rangle\langle n_i|\) at \(\tau_{n+1}\) contribute to the trace, i.e. for each contributing diagram the topmost ket state is identical to the topmost bra state, allowing to flip over from the left to the right side.

As an example, the \(S_3\) rephasing ESA response function evaluated in Hilbert space
takens the following form:

\[ S_3(t_1, t_2, t_3) = \langle \hat{\mu}^- \hat{G}^\dagger(t_1 + t_2 + t_3) \hat{\mu}^- \hat{G}(t_3) \hat{\mu}^+ \hat{G}(t_2) \hat{\mu}^+ \rho(-\infty) \rangle \]  

(3.34)

Propagation backwards in time is achieved using the complex conjugate time evolution operator, \( \hat{G}^\dagger(t) \). Eq. 3.34 is equivalent to the \( S_3 \) term in Eq. 3.14. The only difference is the dipole operations being applied in the Schrödinger and the interaction picture, respectively. The closed time path loop is simply a different way of interpreting the equations. Then, calculating the response functions, as in the Liouville space description, means evaluating a series of dipole operations and propagations of the \( ket \) and \( bra \) wave functions.

In order to describe dephasing and loss of correlation in Hilbert space, the statistics have to be evaluated. This can be done either on the input side, i.e. the Hamiltonian going into the response calculation, or on the output side by evaluating and averaging the response for many molecular trajectories. Examples of both approaches are shown in the following.

### 3.3.2 Cumulant Approximation - Spectral Diffusion

So far, the Hamiltonian describing the interaction free vibrational system \( H_0 \) was assumed to be time independent (see Eq. 3.2 and following). This is of course not strictly correct, since low frequency motions, i.e. the \( bath \), modulate the spectroscopic properties of the high frequency modes probed by the nonlinear spectroscopy. It is these \( slow \) bath modulations of the Hamiltonian that give access to the structural dynamics of the investigated system through spectroscopy.

As a consequence, the time evolution operator \( \hat{G}(t) \) takes the following general form
for a time-dependent system Hamiltonian $\hat{H}_0(t)$ [7]:

$$\hat{G}(\tau_2, \tau_1) = \theta(\tau_2 - \tau_1) \exp_+ \left( -i \int_{\tau_1}^{\tau_2} d\tau H_0(\tau) \right)$$

(3.35)

Here, $\exp_+$ denotes the time ordered exponential. Using this expression and invoking the Condon approximation, i.e. the dipole operator does not depend on the bath motions, the linear response for a single chromophore can be rewritten as:

$$\langle \hat{\mu} - \hat{G}(\tau_2, \tau_1)\hat{\mu}^+ \rho(-\infty) \rangle = \mu^2 \exp(-i\omega_{01}(\tau_2 - \tau_1))$$

$$\times \langle \exp_+ \left( -i \int_{\tau_1}^{\tau_2} d\tau \delta\omega_{01}(\tau) \right) \rho(-\infty) \rangle$$

(3.36)

where the Hamiltonian was separated into the average fundamental transition frequency $\omega_{01}$ and the fluctuations $\delta\omega_{01}(\tau)$ about this average. The trace can be evaluated using the Magnus expansion [113], which in this context is usually referred to as cumulant expansion [7].

$$\langle \exp_+ \left( -i \int_{\tau_1}^{\tau_2} d\tau \delta\omega_{01}(\tau) \right) \rho(-\infty) \rangle \equiv \exp\left( \sum_{n=1}^{\infty} \frac{(-i)^n}{n!} g_n(t_1) \right)$$

$$\equiv \exp(-g(t_1))$$

(3.37)

Eq. 3.37 defines the lineshape function $g(t)$ which fully describes the linear response. By definition of the expansion, each order of the lineshape function $g_n(t_1)$ is an $n$-fold integral over the $n$-point time correlation function of the frequency fluctuations $\delta\omega_{01}(t)$. The first order component $g_1(t) = 0$ by definition of the frequency fluctuations $\delta\omega_{01}(t)$. 
for \( n = 2 \) is:

\[
g_2(t) = \int_{\tau_0}^{t} d\tau_2 \int_{\tau_0}^{\tau_2} d\tau_1 \langle \delta \omega_{01}(\tau_1) \delta \omega_{01}(\tau_0) \rho(-\infty) \rangle
\]

\[
\equiv \int_{\tau_0}^{t} d\tau_2 \int_{\tau_0}^{\tau_2} d\tau_1 C(\tau_1 - \tau_0)
\]

(3.38)

where the frequency correlation function \( C(t) \) was defined.

One of the most important approximations in nonlinear spectroscopy is the assumption that the higher orders of \( g(t) \) vanish, which is called the second order cumulant approximation. Since similar expressions as given here for the linear response can be derived for all other orders of spectroscopy, all spectroscopic observables are then characterized by this lineshape function or the frequency correlation function, respectively.

The cumulant approximation is exact for Gaussian fluctuations of the transition frequencies \([7]\). A number of explicit models for the FCF have been developed that in turn connect the nonlinear response to a microscopic mechanism. The most prominent one is the stochastic model developed by Kubo \([114]\) which assumes Markovian fluctuations of the transition frequencies, yielding an exponentially decaying FCF:

\[
C(t) = \Delta^2 \exp(-t/\tau_c)
\]

(3.39)

This model is quite useful to discuss some of the important concepts encountered in 2DIR spectroscopy. The FCF has two parameters: the amplitude of the frequency fluctuations \( \Delta \) and the decay time of frequency correlations \( \tau_c \). For very slow fluctuations (inhomogeneous limit, \( \tau_c \to \infty, \Delta \tau_c \gg 1 \)), the FCF is constant \( C(t) = \Delta^2 \), resulting in a Gaussian lineshape with line width \( \Delta \). For fast fluctuations (homogeneous limit, \( \tau_c \to 0, \Delta \tau_c \ll 1 \)) the lineshape turns into a Lorentzian with a line width \( \Gamma = \Delta^2 \tau_c \). Since \( \Gamma < \Delta \), the line width gets narrower as the time scale of frequency fluctuations gets faster, a phenomenon generally known as motional narrowing.
Intermediate regimes show an initial frequency correlation that decays with the characteristic time scale $\tau_c$, a phenomenon usually called spectral diffusion. These intermediate regimes are the most interesting ones for 2DIR, since then the spectral diffusion time $\tau_c$ can be related to a structural correlation time. This can be directly observed in the 2DIR spectra as shown in the example Fig. 3.7. The initial elongation of the peak shapes decays with the spectral diffusion time scale $\tau_c$.

A number of other microscopic models have been developed, all sharing the big advantage that the nonlinear response functions can be calculated analytically. An overview of models, the respective correlation functions and their microscopic interpretation is given in Table 1 of Ref. [115]. The multimode Brownian oscillator developed by S. Mukamel [7, 116] is especially important, since it allows a fully quantum mechanical description of the bath and system bath interaction, and can describe important spectroscopic observables like the Stokes shift, i.e. the red shift of the emission spectrum with respect to the absorption spectrum.

Alternatively, the FCF can be obtained from MD simulations with various methods of mapping the MD observables, e.g. electric fields, onto the transition frequencies [91, 92, 117–119]. The resulting transition frequency trajectories are then used to calculate the FCF.

Within the cumulant approximation, the calculation of the third order response functions can be generally solved as a function of the lineshape function $g(t)$ [7, 120]. An example for $S_1$ is given in Eq. 3.40.

$$S_1(t_1, t_2, t_3) = \mu^4 \exp(i\omega_0(t_1 - t_3))$$
$$\times e^{-g^*(t_1)+g^*(t_2)-g^*(t_3)-g^*(t_1+t_2)-g^*(t_2+t_3)-g^*(t_1+t_2+t_3)} \quad (3.40)$$

As a result, calculating the 2DIR spectra is extremely simple and fast. However,
it was soon realized that a number of important mechanisms and processes cannot be described in this limit. It should be noted that the anharmonicity shift of the $1 \rightarrow 2$ transition can only be treated as a constant within this description.

### 3.3.3 Other Models

If the amplitude or the orientation of the transition dipole moments depend on the bath motions, which is called *non-Condon effects*, the cumulant approximation is no longer applicable even if the fluctuations of the dipole moments follow Gaussian statistics. This was for instance found to be of major importance for the hydroxyl (O-H and O-D) stretching motions in isotopically diluted water [121]. Since no analytical solution to the problem is available, the response functions are calculated numerically for many molecular trajectories acquired from MD simulations. For the linear response with $t_n = \tau_{n+1} - \tau_n$,

$$S^{(1)}(t_1) = i e^{-i\omega_0 t_1} \langle \mu(\tau_2)\mu(\tau_1) \rangle \int_{\tau_1}^{\tau_2} d\tau \delta\omega_{01}(\tau) \rangle_{\tau_1} \tag{3.41}$$

where $\mu(\tau)$ is the now time-dependent transition dipole moment magnitude and $\langle \rangle_{\tau_1}$ denotes the averaging over initial conditions. Similar expressions are found for the third order response [121].

For a spectrum composed of discrete decoupled modes, the linear and nonlinear response can be acquired by the *summing over states* (SOS) approach [122–124]. The nonlinear response functions are then calculated from a spectral density subject to bath modulations, rather than from fluctuating transition frequencies. These spectral densities are typically generated from Monte-Carlo or MD snapshots with ab-initio calculations for the vibrational Eigenstates and transition dipole moments. This means, that the explicit dynamics of these Eigenstates are neglected, i.e. interactions and energy exchange between the modes must be small for this model to produce reasonable results. Depending on the molecular system, calculation of the Eigenstates can be computationally
The cumulant approximation can be extended to describe a small number of distinct coupled states (typically 2 or 3) subject to Gaussian fluctuations [13, 125]. By assigning separate lineshape functions to the individual states and the coupling terms. This approach is the simplest phenomenological model to describe coherence transfer, i.e. energy transfer that can conserve correlations.

A fully quantum mechanical theory for stochastic chemical exchange or energy transfer between modes subject to spectral diffusion has been developed, the stochastic Liouville equation [45, 126, 127]. This theory combines the quantum description of bath motions using the multimode Brownian oscillator model with a stochastic transfer or exchange process. It is one of the few examples where it is more convenient to describe the system evolution in Liouville space, see Eq. 3.33. Despite its conceptual beauty, the limitations in applicability of this model are quite severe.

A large body of work from the Mukamel group exists describing the nonlinear response of excitons using the nonlinear exciton equation [7, 123, 128]. Here, the equations of motion for the exciton creation and annihilation operators $\hat{B}^\dagger$ and $\hat{B}$ are expanded in orders of the external electric fields (rather than the time-dependent density matrix) to yield closed sets of equations for each order of spectroscopy. Even though it avoids the computationally demanding calculation of the exciton states (see SOS approach above), the formalism is restricted to Lorentzian lineshapes since it assumes very fast bath motions. Operating in the exciton basis, the model cannot describe nonadiabatic evolution of the exciton states. Following the ideas developed during this work[16] described in Chap. 6, this restriction was most recently overcome by introducing a direct numerical integration scheme similar to the split operator technique [129].

Recently, an approximate description of the dynamics of many coupled chromophores and dynamic excitons was developed [118, 130]. The idea is to separate the time scales of frequency fluctuations into fast components causing motional narrowing and slow
components responsible for spectral diffusion. In this limit, the motional narrowing is described by time averaging of the fluctuating frequencies over a characteristic time scale, usually on the order of the inhomogeneous dephasing time. The time averaged frequency distribution captures the motional narrowing effect quite well. For systems for pronounced intermode coupling, the same idea can be applied to the multimode Hamiltonian, averaging over the fast fluctuations of frequencies and couplings, to acquire motionally narrowed exciton distributions. In the third order response, the averaging is performed during the coherence evolution times $t_1$ and $t_3$. The spectral evolution during population time $t_2$ then captures the slower spectral diffusion components. The method is not particularly accurate in describing the dynamics, it is rather intended to be fast in order to be able to fit experimental data. In particular, the model breaks down for pronounced non-adiabatic interactions during the coherence times.

All of the above methods assume an equilibrium bath with a negligible perturbation from the optical fields. Some work was also done on nonequilibrium dynamics by explicitly introducing the optical field perturbation into a molecular dynamics simulation [131–134]. This model seems to be quite suitable for low frequency motions with $\omega < 1000 \text{ cm}^{-1}$, in particular in simulating the fifth order Raman signal [65]. For higher frequency modes however, the modelling of the spectral evolution is too coarse to accurately reproduce the nonlinear response.

3.3.4 Numerical Integration of the Schrödinger Equation - Fluctuating Disordered Vibrational Excitons

Many of the above approximations are not applicable for vibrational modes in neat H-bonded liquids like water or formamide. This is mainly because in these systems all dynamics, spectral diffusion, intermolecular energy transfer, and population relaxation happen on comparable and very fast time scales.

The resonant interactions between neighboring vibrational chromophores have magni-
tudes comparable to the fluctuation amplitudes of the local transition frequencies. This is caused by the large transition dipole moments and the high density of chromophores producing large intermolecular coupling coefficients through electrostatic transition dipole interactions. This leads to formation of vibrational excitons. The size of these delocalized excitations is however dynamically constrained by local structural fluctuations, resulting in local frequency fluctuations but also strong fluctuations of the vibrational couplings. Such fluctuations can lead to dynamic localization and self-trapping of the excitons, depending on the relative magnitudes of the fluctuations and couplings. Static disorder-induced exciton localization and self trapping is well known in solid state systems. Here the situation is more complicated since the disorder is dynamic, which eventually invalidates the Eigenstate picture for the vibrational modes.

This can be understood by taking a molecular snapshot and exciting the vibrational system into an (instantaneous) Eigenstate. The definition of the Eigenstate or Eigenbasis specifically means that if the system is in an Eigenstate, it will stay in that Eigenstate upon evolution. However, structural fluctuations cause the Eigenstate itself to change. If the changes are small, an adiabatic approximation is applicable where the wave function would simply follow this change. If the changes are big, a diabatic approximation could be applied, where the wave function is unchanged in a local basis. But that means that the system would not stay in an Eigenstate. The truth lies somewhere in between: the evolution of the excitations is inherently non-adiabatic, governed by multiple state crossing. The use of an Eigenstate or exciton basis is therefore not appropriate.

At least for liquid water, the assumption of Gaussian statistics of the local frequency fluctuations is also not valid. The properties of the local vibrational Hamiltonian are strongly modulated by the number and strength of H-bonds. These interactions are highly asymmetric, which leads to a number of asymmetries in the frequency statistics:

1. The distribution of frequencies is not Gaussian and not even symmetric.

2. The time scales of frequency fluctuations depend on the transition frequency.
3. The local anharmonicity shift depends on the transition frequency.

4. The average magnitude and the fluctuations of magnitude and orientation of the transition dipole moments depend on the transition frequency.

The last point is a restatement that the Condon approximation does not hold in water.

The resulting dynamics for disordered vibrational excitons in H-bonded liquids are very complex, and none of the simplified or approximate models for calculating the nonlinear response given in the previous sections are satisfactory. Most recently, an all numerical approach for calculating the response based on Numerical Integration of the Schrödinger Equation (NISE) [16, 90, 110, 135] was developed, which is well suited to describe these dynamics.

The idea behind it is quite simple. First, a multimode Hamiltonian is written in a time-independent basis; in most cases the local (molecular) basis is used. Fluctuations of the Hamiltonian parameters, diagonal frequencies, off-diagonal couplings, etc., are treated explicitly by generating Hamiltonian trajectories from MD trajectories with appropriate mapping of Hamiltonian parameters onto the MD observables, e.g. electric fields. Finally, the propagations of the multimode vibrational system are calculated by numerically integration.

The time-dependent Schrödinger equation:

$$\frac{\partial}{\partial t} \Phi(t) = -i\hat{H}(t)\Phi(t)$$ (3.42)

is solved separately for each excitation level, i.e. ground state, singly excited state, doubly excited state, etc. Here, $\Phi(t)$ is the time-dependent wave function that is expanded in the local basis $|k\rangle$, for singly excited states:

$$\Phi(t) = \sum_k c_k(t)|k\rangle$$ (3.43)
The sum runs over all local vibrational modes considered. Plugging Eq. 3.43 into Eq. 3.42 yields the equation of motion for the wave function coefficients,

$$\frac{\partial}{\partial t} c_k(t) = -i \sum_l H_{kl}(t)c_l(t) \quad (3.44)$$

where the Hamiltonian is also expressed in the local basis, $H_{kl}(t) = \langle k|\hat{H}(t)|l \rangle$. For small time steps $\Delta t$, Eq. 3.44 can be solved iteratively, assuming that the Hamiltonian is constant during this time step.

$$c_k(t + \Delta t) = \sum_l \langle k| \exp\left(-i\hat{H}(t)\Delta t\right)|l \rangle c_l(t)$$

$$\equiv \sum_l \langle k|\hat{U}(t)|l \rangle c_l(t) \quad (3.45)$$

Eq. 3.45 defines the infinitesimal propagator $\hat{U}(t)$. This can be generalized in order to calculate the Greens functions in the Schrödinger picture (Eq. 3.34) by time ordered application of infinitesimal propagations:

$$\hat{G}(\tau_b, \tau_a) = -i\theta(\tau_b - \tau_a) \prod_{\tau=\tau_a}^{\tau_b-\Delta \tau} \hat{U}(\tau). \quad (3.46)$$

The time dependence of the local transition dipole moments is often also mapped from the MD observables in order to calculate the time-dependent coupling coefficients from transition dipole coupling (TDC). This information can also be used straightforwardly to account for non-Condon effects, by explicitly treating the time dependence of the dipole operators in Eq. 3.34.

While this method is capable of describing any complex dynamics of an excitonic system, it has two major drawbacks. First, the fully numerical treatment removes most physical interpretation of the microscopic mechanisms from the simulations. The theory essentially performs numerical experiments. As in the experiments, understanding the
microscopic origins of the calculated signal often requires changing certain parameters and interpreting the change this causes in the signal.

Second, the NISE approach is computationally demanding. In particular, propagations of doubly excited states is extremely costly if more the $\approx 40$ basis states are considered. As a consequence, applications of NISE were restricted up until recently to small systems or linear response calculations $[90, 110]$. It was one of the most important achievements of this work to remove this limitation by introducing the split operator approach $[16, 135]$ that significantly speeds up the calculations making it feasible for many excitonic systems. The details of the simulation protocol are described in great detail in Chap. 6.

### 3.3.5 Population Relaxation and Thermalization

So far, this section focused on the dynamics of the coherences, or the phase relaxation, as it is related to the structural evolution of the sample. And indeed, most theoretical work focuses on these dynamics. Population relaxation on the other hand is poorly investigated theoretically throughout the literature. The only common population relaxation model uses a phenomenological \textit{ad hoc} approach, assuming that the relaxation is a stochastic incoherent process, in which population and energy is transferred to lower frequency modes. In the nonlinear response, this is modelled by simply multiplying the response functions with a exponential relaxation factor $\Gamma$, for instance the third order rephasing response $S_I$ in Eq. 3.15:

$$S_I(t_1, t_2, t_3) = \left( \sum_{k=1}^{3} S_k(t_1, t_2, t_3) \right) \Gamma(t_1, t_2, t_3) = \left( \sum_{k=1}^{3} S_k(t_1, t_2, t_3) \right) \exp \left( -\frac{t_2}{T_1} \right)$$  \hspace{1cm} (3.47)
where $T_1$ is the population relaxation time. If $T_1$ is comparable to the dephasing times, this is often extended to also describe relaxation during the coherence times. In this context, the amplitude decay of the coherence is usually assumed to occur within half the population lifetime.

$$
\Gamma(t_1, t_2, t_3) = \left( -\frac{t_1 + 2t_2 + t_3}{2T_1} \right)
$$

(3.48)

This means that the population relaxation acts as a direct dephasing term for the loss of frequency correlations, as also seen in Eq. 3.29. In some cases, the population relaxation is assumed to be cascaded through the different frequency regions, described by a closed set of rate equations [136, 137].

Up until now, no quantum mechanical description of the population relaxation processes has emerged in the literature. It is clear that this process is determined by the same anharmonic couplings between the vibrational system and the low frequency bath that are responsible for both spectral diffusion and relaxation, since energy conservation requires participation of the bath modes. Certainly, a microscopic quantum mechanical theory could reveal the connections between these two classes of processes.

However, this type of theoretical modelling is extremely challenging, and might only be accessible in the near future. However, the limited theoretical effort is most certainly related to experimental challenges to extract the specifics of the relaxation dynamics beyond a simple ad hoc model. A few attempts have been made to specifically analyze the anharmonic couplings responsible for the relaxation process [138, 139], but the experiments are extremely challenging in being able to dissect this specific information from the data.

Even less explored are thermalization phenomena. It is well known that the vibrational energy deposited with the optical excitations relaxes and eventually thermalizes. This is usually observed by using pump probe spectroscopy, where a thermal signal arises at large $t_2$ values [140–142]. The spectral signature of that signal is usually characterized
by the temperature difference linear spectra, and is often referred to as *hot ground state* [141]. Some attempts were made to describe the dynamics of the thermal signal in a rate equation approach [140], but the results are often not satisfactory.

Additionally, it is expected that even at early population times when the thermalization process is far from being complete, anharmonic coupling between the low frequency modes populated from relaxation and the mode under investigation should lead to a nonlinear signal. The various processes involving intermediate stages of relaxation and thermalization and their impact on the nonlinear signal is very poorly understood and investigated at the moment. No explicit theoretical models exist, and the respective experimental data is, if at all, only analyzed phenomenologically.
Chapter 4

Experimental Details

The experimental requirements for ultrafast vibrational spectroscopy of neat liquids are very challenging. The fast dynamics demand optical pulses shorter than 100 fs in the mid-IR. Vibrational transitions are generally weak compared to electronic transitions and IR detectors are also less sensitive than in the visible. Therefore, pulse energies of at least a few $\mu J$ are needed in order to resolve the nonlinear signals. On the other hand, the transitions are strong enough that for neat water and formamide the thickness of the liquid samples has to be on the sub-$\mu m$ scale to avoid pulse distortion due to high optical densities, a challenge that has long prevented nonlinear spectroscopies of these neat liquids. Finally, since the heterodyne detected signals are extremely sensitive to phase noise or timing jitter between excitation pulses, a reliable scheme for either passive or active phase stabilization is crucial for the success of the experiments. The realization of all these requirements is described in this chapter. While most of the technology was developed in the group, particular attention is paid to the sample cell design and fabrication which was the major contribution of this thesis work.
4.1 Short Pulse Generation

Only a limited number of approaches exist capable of producing < 100 fs, few µJ pulses in the mid-IR [41, 143, 144]. The most common scheme uses an amplified Ti:Sapphire laser system pumping an optical parametric amplifier (OPA) followed by difference frequency generation (DFG) as the final step to generate the mid-IR pulses [143]. Most 2D-IR experiments in the literature use that approach. Small modifications allow mid-IR generation directly in the OPA in some cases [41]. The Ti:Sapphire based systems suffer from significant limitations in pulse energy and bandwidth due to damage thresholds of the laser materials. Extensive effort within the group was directed towards developing scalable mid-IR sources that overcome these restrictions. The most successful scheme is based on optical parametric chirped pulse amplification [144] and is described in great detail in D. Kraemer’s thesis [46]. However, all the experimental results presented within this work were acquired at the Max Born Institute (MBI) in Berlin, Germany, and the European Laboratory for Nonlinear Spectroscopy (LENS) in Florence, Italy. Both labs use IR sources based on commercial Ti:Sapphire systems. The basic principle of these IR sources will be described in the following.

The typical amplified Ti:Sapphire systems produce 50-100 fs, 800 nm pulses at 1 kHz with pulse energies of 0.5-1 mJ. The Ti:Sapphire oscillators are pumped by continuous-wave (cw) intra-cavity doubled solid state lasers at 512 nm and passively mode-locked due to Kerr-lensing [145]. The ~ 50 fs, 80 MHz, few nJ oscillator output is then stretched to several hundred ps. The subsequent regenerative amplifier is based on chirped pulse amplification (CPA) with Pockel cell-switching at 1 KHz. The final step compresses the ~ 1mJ output pulses to 50-100 fs that are used to pump the OPA.

The basic scheme of the OPA and subsequent DFG is shown in Fig. 4.1. Both systems at the MBI and LENS are based on the same design by Kaindl et al. [143]. A small portion of the 800 nm pump is split off to generate white light in a thin sapphire crystal. The remaining pump beam is split again in order to pump the two stages of the OPA. In
a first stage, the white light is collinearly combined with the pump beam and focused into a \( \beta \)-barium borate (BBO) crystal to generate signal and idler beam by parametric amplification with \( \omega_{\text{pump}} = \omega_{\text{signal}} + \omega_{\text{idler}} \). In the second stage, the signal is amplified with the other portion of the 800 nm pump, again also generating the idler to conserve energy and momentum. Signal and idler are then focused into a DFG crystal (often \( \text{Ag}_2\text{GaS} \)) to generate the mid-IR at \( \omega = \omega_{\text{signal}} - \omega_{\text{idler}} \). A more detailed discussion of the mid-IR sources can be found elsewhere \([41, 46]\).

The mid-IR pulses were characterized within the photon echo spectrometer using the non-resonant third order signal from a thin CaF\(_2\) or BaF\(_2\) crystal. The pulse duration can be determined from the spectrally integrated homodyne photon echo signal, see Sec. 3.2.4, and the spectrum is acquired with the monochromator within the echo setup. Alternatively, the IR pulses can be fully characterized by third-order frequency resolved optical gating (FROG) \([146]\). The FROG measurement is useful in particular when
compensating for chirp at the sample position. The Frog traces of a typical chirped and a chirp-free 3μm pulse used for the water experiments (Chap. 5) is shown in Fig. 4.2 a and b, respectively.

Figure 4.2: Typical FROG traces of the 3 μm pulses used 2DIR experiments of water: (a) chirped pulse, (b) chirp-free pulse.

4.2 Infrared Photon Echo Spectrometer

The biggest challenge in heterodyned photon echo spectroscopy is to achieve the required phase stability. The heterodyned signal amplitude and SNR critically depends on a stable phase relationship between the excitation pulses [6]. Phase stability is lost through jitter or inaccuracies of the relative pulse timings, which in conventional optical setups often happens through path length fluctuations between the different arms of the spectrometer, e.g. mirror vibrations and delay line inaccuracies. Ideally, long time phase stability of better than λ/100 is desired.

Most experimental 2DIR approaches have tried to mechanically minimize path length jitter or actively stabilize the relative pulse timings by using Helium-Neon laser interferograms [11, 25, 97, 147, 148]. Most recently, 2DIR spectrometers using pump-probe
geometry (collinear pump pulses) have been proposed \cite{149} and were implemented using pulse shaping technologies \cite{150-152}. These approaches remove the phase stability issue and allow for fast acquisition and easy automation, but require pump probe background subtraction that can distort the final signal. Additionally, the technique is no longer background free and needs respectively stronger excitations to create larger signals.

Passive phase locking using diffractive optics (DO) was originally proposed to remove the need for active phase stabilization in heterodyning of nonlinear signals in the visible \cite{153,154}. The advantages of DO based heterodyne detected nonlinear signals over non-stabilized and actively stabilized approaches have recently been reviewed \cite{6}. The 2D photon echo spectrometer design used in this work is based on the work of Cowan et al. \cite{155}. The setup is shown schematically in Fig. 4.3.

![Diagram of the passively phase-locked 2DIR photon echo spectrometer](image)

Figure 4.3: The passively phase-locked 2DIR photon echo spectrometer, see text. Inset: photon echo phase matching in boxcar geometry. The wave vector projections onto the focal plane are shown, $\mathbf{k}_s = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$. 
The incoming beam is split with a conventional 50/50 dielectric beam splitter optimized for a given spectral range into the pump arm (red, $\mathbf{k}_1$ and $\mathbf{k}_2$) and the probe arm (green, $\mathbf{k}_3$ and $\mathbf{k}_{LO}$). The mechanical delay stage in the probe arm (T delay) introduces the population time delay $t_2$. Both beams are collinear and levelled, and directed onto the first 90° off-axis parabolic mirror (Newport Opticon bare gold, focal length 4") to be focused into the DO. The grating is optimized to split each beam vertically into 1st and -1st order (full and dashed line) with 70% efficiency. The separation of the incoming beams is matched to the vertical separation generated by the DO after recollimation, to produce a square boxcar geometry seen in the inset of Fig. 4.3. A mask is used to block the small contributions from other diffraction orders. A first compensation plate (CP1) in both pump beams ($\mathbf{k}_1$ and $\mathbf{k}_2$) is inserted to compensate for dispersion introduced into the probe arm by the beam splitter. It is helpful to place CP2 after the DO, since then the pump and probe arm are not coincident in time on the DO reducing the chance of laser induced damage of the DO. The small portion reflected off CP1 is used to monitor the laser power before the sample with a single element MCT detector (power 1). Wave plates are inserted into each of the four beams for independent manipulation of the polarization of each excitation pulse.

A second mechanical stage ($\tau$ delay) introduces a delay between the bottom two ($\mathbf{k}_1$ and $\mathbf{k}_3$) and the top two ($\mathbf{k}_2$ and $\mathbf{k}_{LO}$) beams. Two roof mirrors are mounted on top of each other, one being moved by a translation stage. Mechanical stability and alignment of the $\tau$ stage are crucial for the performance of the setup. The four beams are then focused into the sample by a 2”, 90° off-axis parabolic. A small optical density (OD) filter is placed into the LO beam before the sample. It attenuates the LO by 1-2 orders of magnitude and is also used to fine tune the spatial overlap between the LO and the generated signal. To compensate for the chirp introduced by that filter, a second compensation plate (CP2) with anti-reflection coating is placed into the other three beams.
After the sample, the beams are recollimated by a fourth off-axis parabolic mirror. The pump beams $k_1$ and $k_2$ are used to monitor the transmitted laser power with a single element detector (power 2). The nonlinear signal can be measured spectrally integrated using a third single element detector (homodyne echo) or spectrally resolved by focussing the beams into an imaging monochromator with an MCT array (Infrared Systems Development Corp.). A flip mirror allows switching between these two acquisition methods. The MCT array has two horizontal lines of 16 (MBI) or 32 (LENS) elements. The LO and signal are imagined on one line and the probe is imaged on the other line of the array to allow convenient switching between photon echo and pump probe measurements.

It was shown [155] that the passive phase stabilization in this design is achieved through anti-correlated phase noise between pulse pairs. Independent path length fluctuations only occur before the DO, but are identical between pairs $k_1$ and $k_3$ or $k_2$ and $k_{LO}$, respectively. This cancels the total phase noise between the two spectrometer arms allowing the usage of the conventional beam splitter.

Initial alignment is done with a red (632 nm) HeNe laser which can be coupled into the setup with a flip mirror. The DO was designed to have pairs of gratings, one for the IR and one for the HeNe that can easily be interchanged. Once the HeNe is aligned, the IR beam is spatially overlapped with the HeNe beam path using pin holes to have good initial IR alignment, which is then optimized for signal. To avoid absorption from water vapor in air which occurs in both frequency regions studied, the whole setup is enclosed in a plexiglass box and put under dry air environment ($CO_2$ or $N_2$).

For homodyne echo and pump probe (PP) measurements, the two delay stages, $T$ delay and $\tau$ delay, directly correspond to the population time $t_2$ and the coherence time $t_1$, respectively, as introduced in Sec. 3.2. For heterodyne detection, the situation is slightly different since the design of the setup with correlated pulse pairs dictates the relative timing of the LO pulse with respect to the three excitation pulses. This is distinctly different from other 2DIR experimental designs, where the timing of the LO
Chapter 4. Experimental Details

usually is a free parameter. In the DO based design, the temporal position of the LO pulse is automatically scanned along as the relative timings of the excitation pulses is scanned. It always appears $t_1$ after the last excitation pulse $k_3$ by design (before $k_3$ for negative $t_1$). This is experimentally realized by a special delay scanning scheme: for negative coherence times $t_1$, the T delay stage is fixed at a desired population time value $t_2$ and the $\tau$ stage is scanned. For positive $t_1$ however, the geometrical arrangement requires that both stages be scanned simultaneously, i.e. for a given $t_1$ the $\tau$ stage is at $t_1$ and the T stage is at $t_2 + t_1$. This coupling between the stages for positive $t_1$ times requires high precision stages. While this is no serious problem in the IR, the situation is more challenging in the visible but was most recently solved with a similar spectrometer design where the two stages are fully decoupled [156].

4.3 Signal Detection

The most sensitive photo detectors in the mid-IR spectral region are liquid nitrogen cooled photo-resistors made of HgCdTe (mercury cadmium telluride, MCT) and InSb. These detectors measure the intensity of the electric field. The response time of the detectors is fairly short (several ns) but is increased by amplification. Usually a two stage voltage amplification is used: a pre-amplifier (supplied with detector, $\sim x100$) close to the detector is followed by gated integration (e.g. Stanford Research Systems SR250) with a total integration window $\Delta t_{int}$ of a few $\mu$s, synchronized with the laser repetition rate. Effectively, the detection system temporally integrates the intensity of each signal pulse.

$$S \propto \int_{t_0}^{t_0+\Delta t_{int}} dt'|E_S(t')|^2$$

Differential detection is used to improve SNR by chopping the pump beams at 500 Hz and recording the difference signal, with and without pump beams.

For spectrally integrated measurements, the signal of the single element detector
(homodyne echo detector in Fig. 4.3) is recorded as a function of the T delay (PP and transient grating) or as function of the $\tau$ and T delay (homodyne photon echo). The non-resonant signal from CaF$_2$ or BaF$_2$ is used to find the 0 position of the stages. All heterodyne photon echo measurements are performed spectrally dispersed. Since the number of array elements is generally too small to cover the whole spectrum with acceptable resolution, the data acquisition involves scanning the delay stages and also scanning the spectral center position of the monochromator. By spectrally overlapping several array pixels between these different spectral chunks, the full spectrum is recovered for each delay time.

### 4.3.1 Spectral Interferometry

As described in Sec. 3.2.1, the heterodyne detected photon echo signal measures the interference term between the nonlinear signal and the LO field, the spectrally resolved signal on the detector is:

$$I(\nu_3) = |E_{LO}(\nu_3)|^2 + |E_S(\nu_3)|^2 + 2E_{LO}(\nu_3)E_S(\nu_3) \cos(\phi_{LO} - \phi_S + \Delta t \nu_3)$$  \hspace{1cm} (4.2)

The first term, the intensity of the LO, is removed by differential detection. Since the LO pulse is scanned along as $t_1$ is changed, no oscillations in the signal are observed as a function of $t_1$. This is distinctly different from most other experimental realizations of 2DIR and a direct consequence of the passive phase stabilization through correlated pulse pairs. In order to recover the electric field of the echo field and also remove the homodyne signal contribution $|E_S|^2$, the spectral interferogram is generated by introducing an overall shift of the LO oscillator pulse $\Delta t$. This is achieved experimentally through slightly different thicknesses of the OD filter and CP2 in Fig. 4.3. The filter and CP2 plates are chosen such that the LO precedes the excitation pulses, and is therefore not affected by pump induced bleaching of the sample. This LO shift in the time domain causes fringes
in the frequency domain. A typical interferogram is shown in Fig. 4.4. The magnitude of the $\Delta t$ shift results in a given fringe spacing which is optimized for the spectral pixel spacing of the array detector.

![Interferogram](image)

**Figure 4.4:** Typical experimentally acquired interferogram for a 2DIR spectrum. Spectrally resolved heterodyne photon echo signal on the array detector as a function of the coherence time $t_1$. The data is processed in multiple steps (see text) to gain the absorptive 2DIR spectrum.

The extraction of the full third order response and the absorptive component of the 2DIR spectrum in particular has been described in great detail before [46]. In short, the analysis involves multiple steps. First, the complex valued electric field is recovered and the homodyne signal is removed by two Fourier transforms of the interferogram independently for each $t_1$. The first Fourier transform generates a spectrum symmetric about 0 with peaks at the fringe frequency. A supergaussian filter is applied removing the negative frequency peak and the constant ($f=0$, homodyne echo) part. This data is again Fourier transformed to yield the homodyne-free complex-valued interferogram. Second, the LO *along-scanning* and overall shift are reversed through appropriate phase factors resulting in the native oscillations of the signal field along $t_1$ that can now be Fourier transformed to get the excitation frequencies $\nu_1$. The only unknown parameter
at this point is the total (random) phase difference between signal and LO. This total phase is acquired through fitting of the projection of the 2DIR spectrum onto the $\nu_3$ axis to independently measure the PP spectrum for the given population time $t_2$ [155, 157].

### 4.4 Sample Preparation

The strong absorption of the O-H stretching vibration in neat liquid water (absorption length $\sim 1\mu m$) and the amide I in liquid FA ($3-4\mu m$) require particular attention. To avoid distortions of the 2DIR lineshapes due to reabsorption and distortion of the signal fields [158], the optical density in the probed frequency region should not exceed 0.3 corresponding to $< 500nm$ for water and $< 1.5\mu m$ for FA. The creation of such thin liquid films is extraordinarily challenging and has long prevented photon echo experiments on neat water. Squeezing a liquid film between CaF$_2$ windows is difficult but possible. However, the nonresonant signal contribution from these thick windows (usually $\sim 1\ mm$) often masks the fast initial dynamics of the liquid [15]. Free standing liquid films and liquid jets have been realized, but are limited to thicknesses of $> 2\mu m$ [41].

A entirely new approach was brought forth by the Miller group [15] with a specially designed nanofluidic sample cell employing 500 nm thick liquid layers sandwiched between sub-micron thick silicon nitride (SiN) membranes. This technology is used in X-ray spectroscopy and diffraction experiments, albeit with no flow [159]. The extremely thin windows were shown to not generate any nonresonant signal [15]. A schematic of the original design of the nanofluidic cell is shown in Fig. 4.5 (a). The cell consists of two pieces with 800 nm thick SiN windows sandwiched together. A 500 nm thick SiO$_2$ spacer defines the thickness of the sample liquid layer. The windows were fabricated at the Cornell Nanoscale Science and Technology Facility (CNF), by deposition low-stress SiN onto Si wafers and subsequent Si wet etching using KOH. These special SiN membranes have been found to be extraordinarily strong, and won’t break even under
several atmospheres of pressure. A narrow channel was removed from the SiO$_2$ buffer layer that allowed the liquid to be pulled into the cell by capillary forces. The capillary forces are modified by a thin $\sim 5$ nm thermal oxide layer, increasing the wettability of the surfaces. After the cell is filled with liquid, it is sealed with polyepoxide glue.

Even though this design worked for the initial 2DIR experiments [15], it has serious stability and reproducibility issues. The key problem is the flexibility of the SiN membranes that allows for fluctuations of the sample thickness. Small changes in the capillary forces outside the window area lead to strong fluctuations of the sample volume since the membranes easily respond to pressure changes. In this closed design, the window area is the *outlet* of any force fluctuations within the liquid reservoir. A 2x2 mm membrane can bow by up to 50 $\mu$m from external pressure. With the lack of external control over these force fluctuations after sealing, the performance of the nanofluidic cell (stable, 500nm thick liquid layer in the window area over many hours) was limited to *trial and error* type approaches. Temperature changes massively perturbed the system and temperature dependent measurements using this design were extraordinarily difficult to conduct.

To avoid these difficulties and increase reliability, stability and reproducibility of the nanofluidic cell, the design was modified to allow external control of the sample volume. The basic idea was to use the flexibility of the membranes to force the liquid layer into the desired state and then actively stabilize it.

### 4.4.1 Actively Stabilized Nanofluidic Flow Cell

The modified nanofluidic design, referred to as *open design*, is shown schematically in Fig. 4.5 (b) and (c). The fabrication of these *nanocells* is described in the next section, 4.4.2. The capillary channels don’t extend to the edge of the cell anymore but instead are connected to holes in one of the two pieces that allow easy external access to the sample volume. These holes are connected to Teflon tubing via o-rings in a home-built sample holder that clamps the nanocell between two copper plates. The Teflon tubing
Figure 4.5: Schematic of the nanofluidic flow cell. (a) Closed design. After a drop of liquid is drawn into the cell by capillary forces, the cell is sealed. (b) Open design. Input and output connections allow external control over the sample volume at all times. (c) Cross section of the open design. Two pieces with 800 nm thick SiN (1, yellow) membranes machined from Si wafers (2, blue) are sandwiched together. A SiO$_2$ spacer (3, green) defines the thickness of the sample volume. Holes (4) are etched into one of the pieces to connect to outside flow control. Trenches (5) are etched to minimize the high flow resistance area. A thin thermal SiO$_2$ layer (light green) increases wettability of the surfaces to enhance the flow. Not to scale.

on the input port is connected to a infuse/withdraw computer controlled syringe pump (Harvard Apparatus PHD2200). Since the open system facilitates pressure driven liquid flow (opposed to capillary driven in the closed design), the small size of the channels can pose a serious problem. For liquid water using 500 nm thick channels, no flow through the nanocell could be achieved. The flow resistance due to the small geometry in combination with the liquid/SiN/SiO$_2$ interfacial forces was too high. To circumvent this problem, trenches were etched into one of the two pieces, increasing the height of the flow channels to 30-50 µm outside the window area, thus minimizing the high flow resistance area. Even then, the flow resistance was too high since no flow was observed at the maximum
achievable pressures of 2-3 bar.

Acceptable flow resistance was found using 1.5 \( \mu m \) thick channels. The nanocell is flushed by pumping \( \sim 1 \) mL of liquid through the sample volume at high pressures (0.2-0.5 ml/hr flow rates). This provides sufficient sample volume on both ends for the active stabilization and also removes air bubbles that are frequently formed in the initial filling process. The air is simply dissolved under high pressure, any sample contamination is flushed out of the sample volume. The bubble formation can be reduced (but not eliminated) by applying a vacuum from the exit side. The sample volume under these high pressures is 30-50 \( \mu m \) thick, estimated from in situ FTIR measurements. The filling procedure was tested and found to work for FA, as well.

After the initial filling process, the sample volume can be controlled with a syringe pump. Withdraw reduces the sample thickness, infuse increases it. Due to multiple technical factors, the response time of such control varies between a few seconds and several minutes, the latter being more common. It was possible to manually approach the desired sample thickness of 400-500 nm. However, fluctuations in the balancing capillary forces prevent long-time stability at the desired sample thickness without active feedback. At this sample thickness, the membranes are slightly bowed inwards since the edges of the windows are fixed to 1.5 \( \mu m \) thickness. For a most homogeneous sample, a point close to the center of the window was chosen, providing thickness variations of less than 50 nm across the laser focal spot. This is illustrated in Fig. 4.6 in a microscope image of a the nanofluidic sample cell partly filled with liquid water to provide a \( \sim 400 \) nm thick

![Figure 4.6: Microscope image of the window area of a partly filled nanofluidic cell. The interference fringes can be used to estimate the sample thickness.](image-url)
layer. The interference fringes can be used to estimate the sample thickness.

Active stabilization of the sample thickness is achieved with a transmission feedback loop, which is illustrated in Fig. 4.7 (a). The signal ratio of the two power monitors, power 1 and power 2 in Fig. 4.3, is used to monitor the transmission of the sample. With a given laser spectrum and the absorption spectrum of the sample, the desired transmission value is experimentally found by measuring the spectrally resolved laser transmission through the sample. A simple proportional feedback is used and found most effective, with the pump rate of the syringe pump being proportional to the difference of current and set point transmission. The typical pump rates are on the order of 10-20 µL/hr and in most cases the average pump rate is 0. This means that no actual flow through the sample occurs; the feedback only stabilizes the sample volume. With the current design, it is not possible to have significant directed flow through the sample at these small sample thicknesses. A pressure driven flow will always bow out the membranes creating a thicker sample. However, a respective cycle of infusion with a period of stabilization can be used for sample exchange if desired.

The typical behavior of the transmission feedback is shown in Fig. 4.7 (b) and (c). The window area is initially empty (transmission close to 1), which is a common state when no feedback is applied. The feedback program causes an underdamped oscillation of the transmission stabilizing it after \( \sim 10 \) min. In (c), the long time stability with transmission variations of \(<5\%\) over many hours is shown.

For the temperature dependent studies, the specifically designed sample holder was built from copper for good heat conductivity. A large piece of water-cooled copper was used as a temperature bath for an electronically controlled thermo-electric cooler. Additionally, the nanocell was enclosed in a copper box with a small opening to prevent heat loss due to radiation and diffusion. This arrangement allowed for sample temperatures to be varied from -20 to 80°C.
The actively stabilized nanofluidic cell has proven extremely reliable. All the experimental data presented in Chap. 5 was taken, over the course of 3 weeks and at many different temperatures, with a single nanocell. The exact same concept with reduced dimensions is currently being tested for use with time-resolved electron diffraction in the Miller group. Also, a patent and a company startup using this technology are underway.

### 4.4.2 Silicon Micromachining

All the nanocells produced in the course of this work were machined at CNF, Ithaca NY. Most of the work was done together with Maher Harb; additional information can be found in his thesis [160]. In the following, the procedure is described based on the machines available at CNF. With different machines available, the procedure likely needs...
minor modifications. In general, cleanliness during the wafer handling is of extreme importance for a successful nanocell production. Any contamination of the SiN surfaces will lead to dirty membranes that cause massive scattering of the IR beams during the 2DIR experiment and is fatal to a successful measurement.

The process to make the SiN membranes is schematically shown in Fig. 4.8. The first step (a) is the use of a furnace for thin film deposition of low stress SiN, a technique commonly called low pressure chemical vapor deposition (LPCVD) [161]. A batch (25 or 50) of virgin Si wafers is placed into a hot furnace (\(\sim 800^\circ\text{C}\)) and exposed to gaseous chemicals at low pressures. In the case of SiN films, a mixture of ammonia\((\text{NH}_3)\) and dichlorosilane \((\text{SiCl}_2\text{H}_2)\) is flown by the Si wafers. The LPCVD process is extremely slow with deposition rates of only a few \(\text{nm/min}\), but it provides very good homogeneity and structural integrity to the thin films [161, 162]. Other thin film deposition methods cannot provide the desired membrane strength and lead to frequent breaking and loss of the membranes. The optimal thickness for 2DIR experiments of liquid water was found to be 800nm. This optimum is defined by transmission of the IR light which is modulated by Fabry-Perot oscillations as the membrane thickness is changed, and the necessary structural support of the membranes. The SiN layer provides both the membranes and mask for the KOH anisotropic wet etching of Si described below. The amorphous SiN structure has approximately equal atomic parts of Si and N; it is often referred to as silicon-rich SiN.

Steps (b) and (c) are both part of the typical micromachining photolithography. In (b), photo resist P1813 or P1818, 1.3 and 1.8 \(\mu\text{m}\) thick, respectively, is spun on both sides of each wafer after priming the surfaces with a typical primer P10. While the top side is used for the actual photolithography, the bottom side (membrane side) photo resist simply protects the SiN membranes. It is thus important that the photo resist on the membrane side is spun first, since the spinning process leads to contamination of the respective bottom side. The resist is usually hard baked (in oven) for 60 min. at 90°C.
Figure 4.8: Schematic of the SiN membrane fabrication process; micromachining is performed in the following order: (a) furnace deposition of 800 nm low-stress SiN (yellow) on blank polished Si wafers (blue), batch process. (b) photo resist S1813 or S1818 (purple) is spun on each single wafer and baked. (c) Photolithography. UV exposure with photo mask, development removes resist in exposed areas. (d) Dry plasma etching removes SiN in areas not protected by photo resist. (e) All remaining photo resist is removed. (f) Anisotropic wet etching with hot KOH creates windows. Due to the high chemical selectivity, the SiN acts as mask.

Step (c) exposes the photo resist on the top side to UV light for 8 s with a specifically designed photo mask using a Carl Zeiss HTG contact aligner. Since the KOH anisotropic wet etching (see below) is sensitive to the absolute crystal orientation, proper alignment of the photo mask to the wafer flat is crucial. The photo masks were specifically designed for this project using the Tanner L-edit software provided at CNF and manufactured with the PG3600 Mask Writer. A typical mask for making SiN membranes is shown in Fig. 4.9. During development by 2-min immersion in MF-321 solution, the exposed parts of the resist dissolve, leaving the rest of the resist as an etch mask for the next step.

In (d), the SiN exposed by the photo resist removal in (c) is dry-etched by reactive ion etching (RIE) [163] using the Oxford 80 plasma etcher. Up to three wafer surfaces are subjected to a radio frequency (RF) plasma in a reactive gas environment. Since these dry etching processes do not have particularly good chemical selectivity (1:3 SiN vs. photo resist), the resist layer needs to be thick enough to survive an etching process long enough to go through the 800 nm thick SiN layer. In (e), the remaining photo
resist is removed and the wafers are cleaned in hot base and acid baths provided at CNF specifically for that purpose.

The final step (f) for manufacturing the SiN free standing membranes is anisotropic wet etching of the Si using 90°C hot 25% KOH [163]. This technique provides excellent chemical selectivity, etching Si at rates of a few µm/min, SiO₂ at a few Å/min and essentially does not etch SiN [163, 164]. Additionally, the KOH etching is highly anisotropic etching only along the (111) planes of Si. This produces the 54° with respect to the (100) surface of the Si wafers. The etching through the entire ∼350 µm thick wafer takes approximately 2.5 h followed by another 30 min of over-etching to remove any remaining residue from the now free standing membranes. The KOH is a particularly dirty process. Rigorous cleaning with many deionized water baths is essential for spotless membranes. The thin film deposition and etch rates of the processes described are given in Tab. 4.1.

The more complicated design shown in Fig. 4.5 (c) essentially follows the same procedure with some additional steps. Most importantly, the KOH etching of the trenches requires precise alignment of the front side to the back side features which is achieved with the EV620 contact aligner (electronic visions EVG) which allows for backside alignment with better than 10 µm accuracy. The KOH for the bottom pieces is split into two parts: (1) ∼2 h of the membrane KOH (f) and (2) the rest of the membrane KOH after photolithography of the trench side features. The KOH in the second step then etches the bottom and top side simultaneously, finishing the membranes and etching the
trenches.

<table>
<thead>
<tr>
<th>machine</th>
<th>process</th>
<th>main etch/deposition rate</th>
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<tbody>
<tr>
<td>LPCVD furnace</td>
<td>Low stress SiN</td>
<td>2 nm/min</td>
</tr>
<tr>
<td></td>
<td>High Temperature Oxide</td>
<td>0.6-0.9 nm/min</td>
</tr>
<tr>
<td>PECVD GSI</td>
<td>n=1.46 oxide dep.</td>
<td>110 nm/min</td>
</tr>
<tr>
<td>RIE Oxford 80</td>
<td>SiN etch</td>
<td>30 nm/min</td>
</tr>
<tr>
<td>wet KOH 90°C</td>
<td>Si anisotropic etch</td>
<td>2.3 μm/min</td>
</tr>
<tr>
<td>wet BOE 6:1</td>
<td>SiO₂ etch</td>
<td>120 nm/min</td>
</tr>
</tbody>
</table>

Table 4.1: Thin film deposition and etch rates.

The SiO₂ buffer layer defining the spacing between the membranes is deposited with plasma enhanced chemical vapor deposition (PECVD) using the GSI. This deposition technique is much faster than LPCVD, but has to be performed on single wafers. Rapid heating and cooling before and after the deposition can sometimes lead to stress-induced fracture of the wafers, that are more fragile after the KOH etching. For removal of the SiO₂ in the window area, another photolithography step is necessary. Here also precise alignment with the existing features on the wafer is crucial and is done with the EV620. The last step in the overall process is the removal of the exposed SiO₂ using wet 6:1 buffered oxide etch (BOE). A buffer such as ammonium fluoride is added to concentrated hydrofluoric acid to reduce the oxide etch rate for better process control. While having very good selectivity between Si and SiO₂, BOE does attack SiN (etch rate ratio between SiO₂ and SiN is ≈ 50:1). This is no problem for the design discussed here with 800 nm thick SiN, but does get difficult when working with thinner SiN membranes for diffraction experiments.
Chapter 5

Temperature Dependence of the 2DIR Spectrum of Liquid Water

The following chapter describes the major experimental work of this thesis. It is a result of a very fruitful collaboration with the group of T. Elsaesser and E. Nibbering at the Max-Born Institute (MBI) in Berlin, Germany using the fs IR laser system there. All experiments presented were performed at the MBI. The diffractive optics based 2DIR experimental setup was constructed by the Miller group in Toronto and later installed by Miller group members. The experimental alignment, data acquisition and analysis were conducted by the candidate, together with Darren Kraemer and Michael Cowan. The overall interpretations of the experimental findings involved all partners. The supporting theoretical studies presented in Chap. 7 were conducted at the University of Toronto and involved a separate collaboration with the group of Shaul Mukamel at UC Irvine.

The temperature dependence of the 2DIR O-H stretching spectrum of neat liquid water was measured, and revealed important new understanding of the liquid structure and dynamics, in particular at temperatures close to the freezing point. The work was also the first direct experimental proof for the formation of vibrational excitons in liquid water. The challenges in understanding this very new phenomenon heavily inspired the
Theoretical work discussed in Chap. 6, 7 and 8. The results and discussions presented in this chapter were recently published [142].

5.1 Introduction

The microscopic structure of liquid water [2] and fluctuations thereof discussed in Sec. 2.3 are closely related to a variety of its anomalies. In the liquid phase, water molecules form an extended disordered network of intermolecular hydrogen bonds (H-bonds). According to the traditional picture of time-averaged water structure [1, 2], each water molecule can form four H-bonds. At a temperature of 300 K, ~90% of these bonds are formed [2, 4, 44, 52, 55, 165–170]. The H-bond network structure fluctuates on a multitude of time scales between 10 fs and 10 ps. These fluctuations include changes of molecular orientations and distances, the breaking and reformation of H-bonds, and slower rotational motions [44, 165–168], all of which can, in principle, occur with various degrees of spatial correlation between H-bonds in the disordered network.

The vibrational spectra of water reflect the dynamical structure of the H-bond network and, thus, are one of the most direct probes of the underlying interactions [1, 171, 172]. Most studies of liquid H2O have focused on the O-H stretching band, displaying a maximum at 3,400 cm−1 and a broad asymmetric spectral envelope. The band is very intense due to the large transition dipole moment and the O-H stretch vibrations are particularly sensitive to the strength and dynamics of the donated H-bonds. The distribution of H-bond geometries and strengths results in a distribution of O-H stretching frequencies with weakly and strongly bonded O-H stretching oscillators absorbing at high and low frequencies, respectively. However, the distribution of transition frequencies undergoes rapid spectral diffusion because of the fluctuating forces the network exerts on a particular oscillator [173]. Upon H-bonding, the diagonal anharmonicity of the oscillator is substantially enhanced compared with a free O-H group, making the hydrogen-bonded
oscillator much more sensitive to the fluctuating forces. In addition, the resonant transfer of O-H quanta between neighboring oscillators causes both spatial and spectral diffusion. But also the vibrational transition dipoles are modulated by the fluctuating network forces leading to Non-Condon effects [121]. With decreasing temperature, the maximum of the band exhibits an overall red shift and a change in the lineshape. This red shift for lower temperatures points to an overall enhancement of H-bonding and structural correlation.

Nonlinear vibrational spectroscopy in the ultrafast time domain provides highly specific insight into the time evolution of vibrational excitations under the influence of a fluctuating bath [12, 141]. Spectral diffusion and vibrational dephasing in water were first studied using HOD in D$_2$O or H$_2$O as a model system in which diluted O-H or O-D stretching oscillators are embedded in a fluctuating D$_2$O or H$_2$O network [18–25]. Here, no resonant energy transfer between the diluted stretching oscillators occurs on the time scales probed by the ultrafast experiments [174]. The first femtosecond two- and three-pulse photon-echo experiments with homodyne detection of the nonlinear signal from HOD in D$_2$O have revealed an ultrafast, sub-100-fs decay component of the macroscopic third-order polarization, followed by slower sub-picosecond and picosecond kinetic components [21, 22]. The fluctuating electric fields interacting with a hydrogen-bonded oscillator represent the major source of the fastest spectral diffusion components [175–178]. Additional insight originates from measuring vibrational photon echoes with heterodyne detection and deriving 2D spectra from them (2DIR). Frequency correlations extracted from 2D spectra of HOD in H$_2$O or D$_2$O display a decay with sub-50-fs, 400-fs, and 1.4-ps components [23, 25, 179]. Different assignments were made for the fast components, whereas the slowest, largest amplitude component was interpreted as a result of H-bond breaking and making dynamics.

Recently, the first 2DIR study of the O-H stretching vibration of neat H$_2$O was reported in which the resonant transfer of O-H stretching quanta between adjacent
molecules adds another component to the ultrafast dynamics [15]. The initial spectrum was found to be clearly inhomogeneously broadened. However, the initial frequency correlations are lost within 50 – 100 fs under ambient conditions. These very fast time scales of spectral diffusion indicated that the frequency modulation is dominated by the high-frequency librations (hindered rotations) of the intermolecular spectrum. It was argued, though, that the dynamic range of the pure H$_2$O studies is limited by energy transfer effects. At room temperature, the loss in frequency correlations was faster than the energy transfer time of $\sim$ 80 fs. However, it will be shown in Chap. 7 that the observed dynamics are dominated by local frequency fluctuations. The delicate interplay between energy transfer, local structural and frequency fluctuations and correlations in the structure is not fully understood at this point; extensive discussion of these effects is given in Chap. 8.

This chapter reports on the first temperature dependence study of the 2DIR spectra of liquid water over a wide temperature range from 274 to 340 K. Using a nanofluidic cell specifically designed for preparing sub-micrometer-thick water layers (see Sec. 4.4) and femtosecond pulses spectrally covering the full O-H stretching band, pronounced changes of the 2DIR spectra with temperature are observed. At 300 K, an initial loss of frequency correlations occurs on a 50-fs time scale, and resonant intermolecular energy transfer occurs within 80 fs. The spectral diffusion time scales are very sensitive to temperature, whereas the intermolecular energy transfer is unaffected by the temperature change. At 274 K, frequency correlations in the O-H stretch vibration persist beyond $\sim$200 fs through reduced frequency modulations from librational degrees of freedom. At these low temperatures, the frequency correlations persist longer than the energy transfer time, suggesting a delocalization of the O-H stretching excitation over several molecules and, thus, formation of vibrational excitons.
5.2 Results

Echo correlation spectra were taken for population times $t_2=0$, 50, 100, and 200 fs at temperatures between 274 and 340 K. The absorptive component of the echo signal (Fig. 1) has two clear peaks corresponding to the $\nu_{01}$ and $\nu_{12}$ transitions of the O-H stretching oscillator. The positive peak along the diagonal originates from the ground state bleach and stimulated emission involving the $\nu_{01}$ transition, whereas the off-diagonal negative peak reflects absorption of the $\nu_{12}$ transition. Because of vibrational anharmonicity, the latter peak is red-shifted by $\sim 250$ cm$^{-1}$.

![Figure 5.1: Absorptive components of the 2D IR echo spectra of pure liquid H2O for various population times and temperatures, arranged vertically for population times 0, 50, 100, and 200 fs, and horizontally for temperatures of 304, 283, and 274 K. The plots for each set of temperatures are normalized to the peak amplitude of the $\nu_{01}$ transition at $t_2=0$ fs.](image)

Spectral overlap of the two transitions distorts the relative and absolute peak po-
sitions, as well as the peak shapes. With decreasing temperature the peaks become red-shifted along both axes, and the relative intensity of the negative peak increases. At all temperatures, the $t_2=0$ spectra in Fig. 1 are similarly elongated along the diagonal, showing strong initial frequency correlations. With lower temperatures, the shape of the $\nu_{0-1}$ peak tapers increasingly from blue to red. Nevertheless, the antidiagonal width of the spectra is essentially independent of frequency.

Spectral diffusion occurs with different time scales across the spectrum. At 304 K, the red side of the $\nu_{01}$ transition has lost most of the initial frequency correlations by $t_2 = 50$ fs, in agreement with our previous studies [15]. However, on the blue side of the spectrum, the 2DIR lineshape is still elongated along the diagonal. Because of the larger bandwidth and higher central frequency of these pulses compared with the previous measurements [15], the dynamics on the blue side of the spectrum are observed here for the first time. These spectral differences in the lineshape are significantly reduced at $t_2 = 100$ fs and become effectively indistinguishable by $t_2 = 200$ fs. Spectra taken beyond $t_2 = 200$ fs are not shown because the reduced population of excited vibrations and increasing contribution of uncorrelated thermal signal. Spectra were also collected at higher temperatures up to 340 K but were largely indistinguishable from the room temperature results.

Marked changes in the 2DIR spectra occur as the temperature is decreased from ambient conditions, in particular to the $t_2$ evolution thereof. At a temperature of 278 K, the frequency correlation becomes somewhat longer-lived overall, with still different dynamics on the two sides of the spectra. On the red side, the correlation time is now $\sim 100$ fs, on the blue side $\sim 200$ fs. A dramatic change occurs in the spectral response on the red side when the sample temperature is reduced to 274 K, now showing strong frequency correlations that persist out beyond $t_2 = 200$ fs. This is most pronounced in the $t_2 = 100$ and 200 fs 2DIR spectra, which are still clearly elongated along the diagonal. The difference in dynamics between the two sides of the spectrum is much reduced at
this temperature.

Quantification of these dynamics from the 2DIR spectra is generally difficult due to spectral dependence thereof and the distortion of the peak shapes. An ellipticity analysis developed in the group and presented in detail elsewhere [46] confirms the numbers and trends given above. The high-level nonlinear signal calculations presented in Chap. 7 reproduce the same spectral and dynamical trends.

Figure 5.2: Spectrally resolved pump probe dynamics of H$_2$O at 274 K for parallel (a) and perpendicular (b) polarization conditions. The colored traces in (c) and (d) show the dynamics integrated over the spectral ranges indicated by the horizontal arrows in (a) and (b), respectively.

In order to also assess population and resonant energy transfer dynamics, spectrally resolved pump-probe experiments were performed with parallel and crossed polarizations of the pump and probe pulses. In Fig. 5.2, results are shown for a temperature of 274 K as a representative example. The signal for both polarization conditions exhibits a fast exponential decay followed by a rise with a 1.3-ps time constant at later times $t_2$ corresponding to thermalization of the optically deposited energy [15, 140, 141]. The spectral profile of this thermal signal is identical to differential linear spectra at different temperatures [180]. The signal amplitude can be used to estimate the transient laser induced temperature increase of $\sim$10 K. This initial increase corresponds to thermaliza-
tion of the excited sample volume; diffusive energy dissipation leads to a reduction of the thermal signal on ns-time scales. The apparent $t_2$ evolution of the spectral pump probe lineshapes arise only from spectral overlap of the thermal signal and the initial population dynamics.

The fast initial dynamics ($t_2 \leq 200$ fs) for both polarization conditions are caused by population dynamics, that is population relaxation and orientational relaxation of the polarization through resonant vibrational energy transfer. Whereas the former causes rapid decay of both signals, the latter causes a decay of the parallel signal with simultaneous increase in the perpendicular signal strength with increasing $t_2$. Molecular orientational relaxation is significantly slower and does not contribute to these signals. The magic angle and polarization anisotropy signals, Sec. 3.2.3, are constructed to distinguish between these two processes.

Figure 5.3: (a) Spectrally integrated pump probe polarization anisotropy at different temperatures. The dashed lines indicate the time resolution of the experiments. (b) Population relaxation times (circles, fitted from magic angle signal) and energy transfer times (squares, fitted from (a)) as a function of temperature. The energy transfer times are unaffected by temperature within the SNR. Population relaxation times are reduced with decreasing temperature.

The spectrally integrated pump probe polarization anisotropy traces for different tem-
peratures are shown in Fig. 5.3 (a). The observed dynamics are unaffected by temperature within the SNR as confirmed by the 80±15-fs single exponential decay fit results shown as squares in Fig. 5.3 (b). Also shown as full circles are the population relaxation times $T_1$ fitted from spectrally integrated magic angle pump probe dynamics, after subtracting the thermal contribution from the signal. The population lifetimes decrease with decreasing temperature, in good agreement with previous studies [181].

5.3 Discussion

Three major types of processes of interactions of the molecular network with the O-H stretching motions contribute to the spectral diffusion dynamics observed in the 2DIR spectra, Fig. 5.1. Similar to isotopically substituted systems, the strength of a donated H-bond (i) determines the frequency of the local O-H stretching oscillator. Intramolecular couplings (ii) between the two O-H stretching modes of an isolated water molecule cause a splitting of the two degenerate O-H stretching motions into a symmetric mode and an antisymmetric mode. Resonant intermolecular couplings (iii) lead to intermolecular vibrational energy transfer and can, depending on the magnitude of the couplings in comparison to the fluctuating forces in the network, lead to coherent delocalization of the vibrational excitations. The fast modulations in the H-bonded structure connect the network dynamics to the dynamics of the spectroscopic observables through all three processes.

The effect of H-bonding on the frequency of an isolated O-H or O-D stretching oscillator (i) above has been studied in detail in isotopically substituted systems [18–25]. The H-bond generally increases the anharmonicity of the O-H potential, lowering its fundamental frequency and making it more susceptible to structural fluctuations. After initial assignment of the direct correlation H-bond length to the O-H or O-D transition frequency [44, 182], later studies revealed also O-H(D)···O angular dependence of the
H-bond strength modulating the transition frequencies [178]. The observed spectral diffusion dynamics of isolated O-H or O-D oscillators are therefore assigned to these local H-bond motions. The distinction between angular and longitudinal motions is made based upon the different time scales of the respective low frequency intermolecular network motions, librations and H-bond stretching, respectively. The dynamics are, however, dominated by the slower 1-ps longitudinal H-bond modes and H-bond breaking dynamics. Librations only contribute to the early spectral dynamics with limited amplitude. Some recent studies with improved time resolution focus on the spectral dependence of these librational contributions to investigate weakly H-bonded, highly transient network states [168, 179].

Additionally, the intramolecular coupling (ii) is modulated by H-bonding. Both fundamental transition frequencies are lowered and mix through the increased anharmonicity of the potentials [135]. The symmetric component can resonantly interact with the HOH bending overtone through a Fermi resonance, enhancing the major population relaxation channel [136]. The asymmetry between the two donated H-bonds adds another component to the interaction, further increasing the mixing between the gas phase Eigenstates [135]. Thus, a clear distinction between symmetric and antisymmetric vibrations no longer holds in the liquid state. Most importantly, both transition frequencies are much more sensitive to correlated or uncorrelated H-bond motions through the respective modulation of the intramolecular couplings, rather than to motions of an individual H-bond.

Finally, resonant intermolecular interactions occur on similar rapid time scales as evident from Fig. 5.3. Depending on the delicate balance of local fluctuations and intermolecular coupling strength, phase correlations can be conserved in the energy transfer process. In these cases, the spectra report on the dynamics of delocalized or excitonic states and the respective time scales can be correlated with structural evolution on length scales spanned by the excitonic wave functions.

The 2D spectra in Fig. 5.1 exhibit two major effects that should be addressed in light
of the above:

- At ambient conditions, the spectral diffusion dynamics on the red side of the 2D spectrum are significantly faster than on the blue side of the spectrum. The high-frequency part of the linear O-H stretching absorption has been attributed to water molecules with non- or weakly hydrogen-bonded O-H groups \[176, 183\]. A similar picture has been developed for the high-frequency part of the 2D spectra of HOD in D\(_2\)O \[121\]. Free or weakly hydrogen-bonded O-H stretching oscillators display a diagonal anharmonicity and a \(\nu_0-1\) transition dipole that are substantially smaller than in a hydrogen-bonded geometry, as is evident from studies of water monomers in nonpolar solution \[184\]. The reduced anharmonicity results in a reduced modulation of vibrational transition frequencies by fluctuating electric fields, and thus spectral diffusion slows down. In addition, the rate of resonant intermolecular energy transfer, a process contributing to vibrational dephasing and spectral diffusion, becomes smaller because of the reduced dipole-dipole coupling. In contrast, free O-H groups are a short-lived species because the reformation of broken H-bonds at ambient temperature occurs on a time scale of <200 fs \[168, 185\]. Hydrogen bond reformation is connected with a jump of the vibrational transition frequency, i.e. spectral diffusion, and consequently the reformation time sets an upper limit for the time scale of frequency randomization in the high-frequency part of the spectrum.

- With decreasing temperature, spectral diffusion slows down, as is evident from the slower reshaping of the spectra for temperatures of 274 and 278 K. Previous studies of neat water \[15\] and HOD in H\(_2\)O/D\(_2\)O \[185\] suggest that the fastest decay of spectral and thus structural correlation is due to librational degrees of freedom that are thermally excited in the fluctuating equilibrium geometry of the H-bond network. At 304 K, such decay occurs on a sub-50-fs time scale, roughly corresponding to the period of librational excitations between 650 and 1,000 cm\(^{-1}\), i.e.
in the range of the librational L2 band of water [1, 136, 171]. The thermal population of excited librational states in this range is reduced by a factor of \(\sim 1.5\) when going from 304 to 274 K. Moreover, the L2 band narrows and shifts to somewhat higher frequencies with decreasing temperature, leading to a substantial decrease of spectral density between 200 and 700 cm\(^{-1}\)[186]. Here, it is important to note that the number of H-bonds only increases by \(\sim 10\%\) in going from room temperature to the lowest temperature. This increase results in a larger fraction of water molecules forming four H-bonds. The decrease in temperature significantly decreases the thermal population of librations above 200 cm\(^{-1}\) that give rise to the fast dephasing [15]. The decrease in thermal occupation of these librations more than compensates for the relatively smaller change in the collective degree of H-bonding that acts to increase the length scale of the frequency correlations. The net effect is slower spectral diffusion at lower temperatures. In addition to slowing down the initial decay component, the subsequent (sub)picosecond loss of spectral correlation may also change but cannot be probed much beyond the 200-fs lifetime of the O-H stretch.

The temperature dependence of the O-H stretch population relaxation times shown in Fig. 5.3 (b) are mostly due to the temperature induced change of the Fermi resonance with the HOH bending overtone. Vibrational populations in the first excited O-H stretching state anharmonically couple to the HOH bending motion. This is the main channel of vibrational relaxation, as the bending overtone further relaxes stepwise into fundamental bending motions, librational motions and eventually thermalizes in the low frequency region of water [136]. The H-bonding induced reduction of the symmetry conditions of the Fermi resonance through symmetric/antistymmetric mode mixing is more than compensated for by the increased spectral resonance. The bending mode blue-shifts with H-bonding while the stretching modes red shift, leading to a spectral overlap between the bending overtone and the red part of the stretching spectrum at ambient conditions. The
temperature dependence of the resonance condition is thus caused by the opposite shift of the interacting bands responsible for the relaxation, increasing the energy mismatch with increasing temperature. These results are in good agreement with previous studies [181].

The decay of the pump probe polarization anisotropy in Fig. 5.3 (b) is unaffected by the temperature change and occurs faster than vibrational energy relaxation at all temperatures. The polarization anisotropy decay is assigned to resonant vibrational energy transfer to neighboring water molecules with random orientation, likely mediated through transition dipole coupling (TDC) [20]. Other possible sources of loss of polarization anisotropy are intramolecular transfer processes and molecular reorientations. The latter are much slower than the observed time scales and can be neglected in pure water dynamics [187]. The former has recently been invoked to explain the depolarization dynamics of water monomers with clear symmetric and antisymmetric modes [188]. Because of the H-bonding induced mixing between these states in neat water, this effect plays a minor role here. Fast initial librational motion of the excited water molecule does contribute to the early depolarization dynamics in isotopically diluted water systems but was recently shown to be insignificant in the presence of intermolecular couplings [16]. Rapid fluctuation of the transition dipole moment orientations induced by bath fluctuations were found to also contribute to the depolarization [135]. Still, the depolarization dynamics are dominated by resonant intermolecular vibrational energy transfer.

It is interesting to compare the time scales of the resonant energy transfer to the spectral diffusion dynamics in Fig. 5.1 for different temperatures. At ambient conditions, the overall spectral diffusion is faster or comparable to the energy transfer times. In this limit, the transfer process is a mainly incoherent process since the phase of the vibrational excitation is scrambled on transfer time scales. In that sense, the energy transfer constitutes an additional component to the rapid loss of frequency correlations in addition to the modulations through high-frequency librations. In other words, under
these conditions the spatial correlation of the vibrational excitation probed in the 2D spectra is very short and is insensitive to fluctuations beyond the first solvation shell about the initial excitation. At lower temperatures however, the spectral correlations persist well beyond $t_2=200$ fs and therefore also well beyond energy transfer time scales. This means that the distribution of transition frequencies, and thus acceptor frequencies, shows only moderate changes on the time scales of the energy transfer. In this limit, the spatial correlation length of the O-H stretching excitation extends over a group of molecules. In other words, the initial stretching excitation is delocalized and the energy transfer process must be an at least partially coherent process.

No theoretical prediction on dynamics of spatial correlations in the disordered H-bond network of liquid water has been presented to date. A minimum correlation length can, however, be estimated considering an incoherent energy transfer within the time scale where the spectral diffusion has not yet scrambled the transition frequencies. In this

Figure 5.4: Spatial correlation length scale probed by 2DIR at 274 K, compared to the average interatomic distance of 2.8 Å. Assuming simple diffusive motion of the excited vibrational energy, the ratio of spectral diffusion vs. energy transfer time gives a minimum of 15 water molecules coherently involved in the vibrational excitation. Taken from [142]
picture, individual incoherent transfer events sample a certain part of the molecular network, the dimension of which is taken as the lower limit estimate of the spatial correlation length. Using this approach with a sampling time of 200 fs and energy transfer time of 80 fs, a minimum spatial correlation length of 4.4 Å is derived at the lowest temperature of 274 K, corresponding to ~15 water molecules. This correlation length is schematically depicted in Fig. 5.4.

Here, it is important to emphasize that this study constitutes the first experimental determination of the correlation length scale for any liquid. The specific nuclear configuration defining a particular frequency has a related length scale. In other words, for every temporal correlation in the liquid structure there is an associated length scale. It can well be appreciated that there is a certain number of molecules that define a particular local field and thereby the frequency of the probed transition. Most theoretical treatments eliminate these microscopic features as phenomenological parameters characteristic of the liquid. At the extreme case, mode coupling theory uses ensemble averaged density fluctuations as the parameterized variable. All semblance of the microscopic structure and dynamics is lost. In the case of MD simulations, it has not been possible to cast an observable that can relate to the microscopic details. There are too many details and statistics to give this information.

In this work, we have deliberately exploited the spatial propagation of the excited vibrations in water in order to sample the energy landscape of the liquid, providing the first direct determination of the (minimum) correlation length of the excitation imposed in the dynamic structure of water. As shown in Chap. 7 and Chap. 8, it is now possible to use MD simulations to analyze this observable within the timescale of the frequency correlations. This should in particular help to refine the temperature dependence of the intermolecular potentials used in MD simulations. These potentials are highly optimized for room temperature and often fail to describe the temperature dependence of microscopic processes. The extreme temperature sensitivity of the 2DIR spectrum and
related spatial correlations will provide an excellent benchmark for improvement of the MD potentials.

5.4 Summary

The results suggest that ultrafast librational fluctuations within the H-bond network dominate the initial loss of frequency correlations of the O-H stretch vibrations at most temperatures. At temperatures near freezing, however, an increased spatial correlation in the network preserves the frequency correlations. This effect is mainly attributed to marked changes in the population and spectral density in the librational L2 band leading to, most importantly, coherent delocalization or formation of vibrational excitons at these low temperatures. The ratio of spectral diffusion and resonant energy transfer time scales is used to give the first direct measure of the (minimum) spatial correlation length scale in the liquid structure within the time window probed by the 2DIR experiment.

A better understanding of the observed spectral dynamics in pure water and the microscopic mechanism that lead to energy redistribution and spectral diffusion requires new theoretical modelling that include the dynamics of the network of H-bonds, energy transfer processes, and anharmonic couplings sensitive to the intermolecular potential. The first theoretical model of the 2DIR response capable of describing the aforementioned effects was developed as part of this work. The simulation protocol is described in Chap. 6 and the results for the simulations of the O-H stretch mode in liquid water are discussed in Chap. 7.
Chapter 6

Simulation Protocol

This section describes the simulation protocol developed during this work in close collaboration with Shaul Mukamel, UC Irvine, in order to calculate the nonlinear response of disordered vibrational excitons. It is based on the NISE approach (see Sec. 3.3.4) which up until now is the only theoretical method capable of satisfactorily treating the complex dynamics encountered in neat liquids. This protocol was used for the simulations presented in Chap. 7 and 8 to calculate the nonlinear vibrational response of liquid water and formamide, respectively. The presented simulation protocol is very general, though, and was published recently [135]. The most important contribution from this work was the introduction of the split-operator technique, Sec. 6.2.1, that reduces the computational cost of these simulations significantly. Only this new development allowed the first explicit theoretical treatment of vibrational couplings in the nonlinear vibrational response in liquid water presented in Chap. 7.

6.1 Vibrational Hamiltonian

A system of $M$ floating coupled vibrational oscillators described by the Hamiltonian
Chapter 6. Simulation Protocol

\[ \hat{H}(\tau) = \hat{H}_S(\tau) + \hat{H}_I(\tau) \] (6.1)

is considered, where \( \hat{H}_S \) represents the vibrational system and \( \hat{H}_I \) contains the interaction with the optical fields. The vibrational system is described by the effective Hamiltonian:

\[
\hat{H}_S(\tau) = \sum_m \omega_m(\tau) \hat{B}_m^\dagger \hat{B}_m + \sum_{m' \neq m} J_{m,m'}(\tau) \hat{B}_m^\dagger \hat{B}_{m'}^\dagger + \sum_{mn,m'n'} V_{mn,m'n'}(\tau) \hat{B}_n^\dagger \hat{B}_m^\dagger \hat{B}_{m'} \hat{B}_{n'} \] (6.2)

Applying the Born-Oppenheimer approximation [189] to separate the high frequency vibrations and the low frequency bath motions, all bath interactions are incorporated into the Hamiltonian parameters. The first two terms describe the free harmonic system, where \( \omega_m(\tau) \) is the fundamental transition frequency of mode \( m \), \( \hat{B}_m^\dagger (\hat{B}_m) \) is the Boson creation (annihilation) operator for mode \( m \), \( [\hat{B}_m^\dagger, \hat{B}_n] = \delta_{m,n} \). The second term contains the intermode coupling \( J_{m,m'} \). The last term describes quartic anharmonicities \( V \). Most commonly, only diagonal anharmonicities of local overtones \( V_{mm,mm} \) are considered. These give the anharmonicity shift between the \( 0 \rightarrow 1 \) and \( 1 \rightarrow 2 \) transitions. However, the above Hamiltonian allows for a description of combination band frequency shifts \( V_{mn,mn} \) and coupling anharmonicities (off-diagonal elements of \( V \)) as well.

The dipole operator is given by:

\[
\hat{\mu}(\tau) = \sum_m \mu_m(\tau)(\hat{B}_m^\dagger + \hat{B}_m) + \sum_{mn,m'n'} \Delta \mu_{mn,m'n'}(\tau)(\hat{B}_n^\dagger \hat{B}_{m'}^\dagger \hat{B}_m + \hat{B}_m^\dagger \hat{B}_m \hat{B}_{m'} \hat{B}_{n'}) \] (6.3)

Here, \( \mu_m \) is the fundamental \( 0 \rightarrow 1 \) transition dipole moment of mode \( m \), and \( \Delta \mu \) rep-
represents the dipole moment anharmonicities. In the Condon approximation, the time averaged amplitudes $\langle |\mu| \rangle_\tau$ are used, neglecting fluctuations and anharmonicities of the transition dipole moments. Non-Condon effects can be included [121] by explicitly treating the bath influence and time dependence of $\mu_m$. The second term in Eq. 6.3 allows for treatment of anharmonicities of the local $1 \rightarrow 2$ transition dipole moments $\Delta \mu_{mmm}$, as well as anharmonicities of dipole moments involving intermode combination bands (other elements of $\Delta \mu$).

### 6.2 Calculation of the Nonlinear Response Functions

The third order contribution to the system’s polarization induced by the laser fields can be written as [7, 190]:

$$P^{(3)}(r, \tau_4) = \int \int \int d\tau_3 d\tau_2 d\tau_1 S(\tau_4, \tau_3, \tau_2, \tau_1) \times$$

$$\times E(r, \tau_3)E(r, \tau_2)E(r, \tau_1),$$

(6.4)

where $S(\tau_4, \tau_3, \tau_2, \tau_1)$ is the third order response function.

$$S(\tau_4, \tau_3, \tau_2, \tau_1) = i^3 \langle \hat{\mu}(\tau_4)[\hat{\mu}(\tau_3), [\hat{\mu}(\tau_2), \hat{\mu}(\tau_1)]] \rangle$$

(6.5)

Sorting out the possible time orderings and invoking the rotating wave approximation, $S$ can be written in terms of Liouville pathways for the different signal directions. This work will focus on $k_I = -k_1 + k_2 + k_3$ and $k_{II} = k_1 - k_2 + k_3$, also referred to as rephasing and non-rephasing pathways, respectively, represented by the double sided Feynman diagrams given in Fig. 6.1. The respective Green’s function expressions for the $k_I$ pathways ($S_1, S_2, S_3$) and the $k_{II}$ pathways ($S_4, S_5, S_6$) are given in Eqs. (6.6). These diagrams are often referred to as ground state bleach (GSB, $S_1$ and $S_4$), excited state emission (ESE, $S_2$ and $S_5$), and excited state absorption (ESA, $S_3$ and $S_6$).
Figure 6.1: Double sided Feynman diagrams for the $k_I$ ($S_1 - S_3$) and $k_{II}$ ($S_4 - S_6$) phase matching conditions, see text. The red arrows indicate the closed time path loops used to calculate the contributions from these diagrams.

\[
\begin{align*}
S_1 &= -\langle \hat{\mu}^-(\tau_1)\hat{G}_{1}^\dagger(\tau_2, \tau_1)\hat{\mu}^+(\tau_2)\hat{G}_{0}^\dagger(\tau_4, \tau_2)\hat{\mu}^-(\tau_4)\hat{G}_{1}(\tau_4, \tau_3)\hat{\mu}^+(\tau_3) \rangle \\
S_2 &= -\langle \hat{\mu}^-(\tau_1)\hat{G}_{1}^\dagger(\tau_3, \tau_1)\hat{\mu}^+(\tau_3)\hat{G}_{0}^\dagger(\tau_4, \tau_3)\hat{\mu}^-(\tau_4)\hat{G}_{1}(\tau_4, \tau_2)\hat{\mu}^+(\tau_2) \rangle \\
S_3 &= -\langle \hat{\mu}^-(\tau_1)\hat{G}_{1}^\dagger(\tau_4, \tau_1)\hat{\mu}^-(\tau_4)\hat{G}_{2}(\tau_4, \tau_3)\hat{\mu}^+(\tau_3)\hat{G}_{1}(\tau_3, \tau_2)\hat{\mu}^+(\tau_2) \rangle \\
S_4 &= -\langle \hat{\mu}^-(\tau_4)\hat{G}_{1}(\tau_4, \tau_3)\hat{\mu}^+(\tau_3)\hat{G}_{0}(\tau_3, \tau_2)\hat{\mu}^-(\tau_2)\hat{G}_{1}(\tau_2, \tau_1)\hat{\mu}^+(\tau_1) \rangle \\
S_5 &= -\langle \hat{\mu}^-(\tau_2)\hat{G}_{1}(\tau_3, \tau_2)\hat{\mu}^+(\tau_3)\hat{G}_{0}(\tau_4, \tau_3)\hat{\mu}^-(\tau_4)\hat{G}_{1}(\tau_4, \tau_1)\hat{\mu}^+(\tau_1) \rangle \\
S_6 &= -\langle \hat{\mu}^-(\tau_2)\hat{G}_{1}(\tau_4, \tau_2)\hat{\mu}^-(\tau_4)\hat{G}_{2}(\tau_4, \tau_3)\hat{\mu}^+(\tau_3)\hat{G}_{1}(\tau_3, \tau_1)\hat{\mu}^+(\tau_1) \rangle \\
\end{align*}
\]
The Green’s functions $\hat{G}_0, \hat{G}_1, \hat{G}_2(\tau_b, \tau_a)$ propagate the ground, the singly excited, and the doubly excited state, respectively, from $\tau_a$ to $\tau_b$. The complex conjugate operators $\hat{G}^\dagger$ respectively propagate backwards in time. The dipole excitation and deexcitation operators $\hat{\mu}^+$ and $\hat{\mu}^-$ are derived from Eq. 6.3 and are given by:

$$\begin{align*}
\hat{\mu}^+(\tau) &= \sum_m \mu_m(\tau) \hat{B}^\dagger_m + \sum_{mnm'} \Delta\mu_{mmnm'}(\tau) \hat{B}^\dagger_n \hat{B}^\dagger_{m'} \hat{B}_m \\
\hat{\mu}^-(\tau) &= \sum_m \mu_m(\tau) \hat{B}_m + \sum_{mnm'} \Delta\mu_{mmnm'}(\tau) \hat{B}^\dagger_m \hat{B}_{m'} \hat{B}_n.
\end{align*}$$

(6.7)

The third order response functions for the two techniques are given by the sum of the respective diagrams:

$$\begin{align*}
S_I &= S_1 + S_2 + S_3 \\
S_{II} &= S_4 + S_5 + S_6.
\end{align*}$$

(6.8)

Harmonic systems ($V \equiv 0$ in Eq. 6.2 and $\Delta\mu \equiv 0$ in Eq. 6.3) are linear; these contributions then cancel exactly and the signals vanish. The finite nonlinear response is induced by the anharmonicities $V$ and $\Delta\mu$.

The response functions in Eq. 6.6 are evaluated by a series of dipole operations and propagations of the many body wave functions as indicated by the closed time path loops in Fig. 6.1, see Sec. 3.3.1. The challenging tasks in these operations are the propagations, in particular for doubly excited states in diagrams $S_3$ and $S_6$.

### 6.2.1 Split Operator Approach

All propagators are calculated using NISE [16, 90, 110], see section 3.3.4 for details.
\[ G(\tau_b, \tau_a) = -i \theta (\tau_b - \tau_a) \prod_{\tau = \tau_a}^{\tau_b - \Delta \tau} \exp \left( -i \hat{H}(\tau) \Delta \tau \right). \] (6.9)

Trajectories of infinitesimal propagators \( \hat{U}(p) = \exp \left( -i \hat{H}(p) \Delta \tau \right) \) are calculated, and the wave functions are then propagated step wise. Setting the ground state energy to zero, the ground state propagator is simply unity. The infinitesimal propagators \( \hat{U} \) can now be expressed in the local basis for the singly \((U^{(1)})\) and doubly \((U^{(2)})\) excited states as given in Eq. 6.10,

\[
U^{(1)}_{m,n}(p) = \langle m | \hat{U}(p) | n \rangle \\
U^{(2)}_{mn,m'n'}(p) = \langle m, n | \hat{U}(p) | m', n' \rangle, \tag{6.10}
\]

where \(|m\rangle = \hat{B}_m^\dagger |0\rangle\) and \(|m, n\rangle = \frac{1}{\sqrt{1+\delta_{mn}}} \hat{B}_m^\dagger \hat{B}_n^\dagger |0\rangle\). For not too large systems, \(U^{(1)}\) can be calculated exactly by diagonalizing the single particle Hamiltonian \(\langle m | \hat{H}_S | n \rangle\), where the third term in Eq. 6.2 does not contribute.

However, propagation of doubly excited states \(|m, n\rangle\) is more challenging due to the large size of the symmetrized two particle basis being \(M(M + 1)/2\). For \(M \geq 40\), direct diagonalization and data storage is computationally too expensive. Instead, the split operator method \([16, 191]\) is used for calculating these matrix exponentials. The Hamiltonian is split into the harmonic part \(\hat{H}_0\) (first two terms in Eq. 6.2) and anharmonic part \(\hat{H}_a\) (third term) and the matrix exponential is calculated as given in Eq. 6.11.

\[
U^{(2)}_{mn,m'n'} = \sum_{m''n''} U^{(2)}_{0,mn,m''n''} U^{(2)}_{a,m''n'',m'n'} \\
= \sum_{m''n''} \langle m, n | \exp \left( -i \hat{H}_0 \Delta \tau \right) | m'', n'' \rangle \times \\
\times \langle m'', n'' | \exp \left( -i \hat{H}_a \Delta \tau \right) | m', n' \rangle \tag{6.11}
\]
The harmonic exponential $U_0^{(2)}$ can be calculated exactly from the single particle propagators, see Appendix A. The anharmonic part is usually small enough to allow first order Taylor expansion. The split operator technique gives good accuracy provided the time steps $\Delta \tau$ are small enough.

It should be noted that in Eq. 6.11 one can avoid computationally expensive matrix multiplications. Consecutive propagation of the doubly excited states with the two infinitesimal propagators $U_a^{(2)}$ and $U_0^{(2)}$ is significantly faster.

### 6.2.2 Linear IR Response

The linear response function $S^{lin}$ within the NISE formulism is given by:

$$S^{lin}(t_1 = \tau_2 - \tau_1) = \langle \hat{\mu}^-(\tau_2) \hat{G}^\dagger_1(\tau_2, \tau_1) \hat{\mu}^+(\tau_1) \rangle$$

(6.12)

The IR absorption spectrum is given by the imaginary part of the Fourier transformation of Eq. 6.12:

$$S^{lin}(\omega) = \Im \left[ \int_0^\infty dt_1 \exp i\omega t_1 S^{lin}(t_1) \right]$$

(6.13)

Through the NISE approach, Eq. 6.13 fully accounts for non-adiabatic exciton evolution, motional narrowing and non-Condon effects in the IR absorption line shape. Calculation of the linear response is extremely fast compared to the 3rd order calculations. A linear spectrum with reasonable SNR can be acquired within a few hours on a single CPU machine.

### 6.3 Nonlinear Signal

If the optical pulses are short compared to the system dynamics, the nonlinear polarization can be described in the impulsive limit. Then, the third order signal along the $k_I$
direction is given by Eq. 6.14 with \( t_i = \tau_{i+1} - \tau_i \).

\[
S^{k_i}(t_1, t_2, t_3) = \sum_{k=1}^{3} S_k(t_1, t_2, t_3) + \sum_{k=4}^{6} S_k(-t_1, t_2, t_3)
\]  
(6.14)

The two-dimensional infrared (2DIR) correlation spectra are obtained by double Fourier transformation with respect to \( t_1 \) and \( t_3 \), with:

\[
S^{2D}(\omega_1, t_2, \omega_3) = \Im \left[ \int \int dt_1 dt_3 e^{i\omega_1 t_1} e^{i\omega_3 t_3} S^{k_i}(t_1, t_2, t_3) \right].
\]  
(6.15)

Similarly, the pump probe (PP) signal in the impulsive limit is given by Eq. 6.16 with \( t_1 = 0 \). Then, the rephasing and non-rephasing contributions are identical. The spectrally resolved PP response is given by Eq. 6.17.

\[
S^{PP}(t_2, t_3) = 2 \sum_{k=1}^{3} S_k(0, t_2, t_3)
\]  
(6.16)

\[
S^{PP}(t_2, \omega_3) = \Im \left[ \int_0^\infty dt_3 e^{i\omega_3 t_3} S^{PP}(t_2, t_3) \right]
\]  
(6.17)

In the impulsive limit, the PP signal is also known as heterodyne transient grating.

The polarization anisotropy (PA) \( S^{PA}(t_2) \) is calculated from the PP signal with parallel (||) and crossed (⊥) polarization of the pump and probe pulses. This is done using the respective projections of the transition dipole moment vectors in Eq. 6.3 in the lab frame when calculating the nonlinear response functions. Orientational averaging is done numerically.

\[
S^{PA}(t_2) = \frac{S^{||}^{PP}(t_2) - S^{\perp}^{PP}(t_2)}{S^{||}^{PP}(t_2) + 2S^{\perp}^{PP}(t_2)}
\]  
(6.18)
Eq. 6.18 can be evaluated for either spectrally resolved or spectrally integrated PP, using the respective PP signals as input.

Similarly, the magic angle (MA) pump probe signal can be obtained spectrally resolved or spectrally integrated.

\[ S_{MA}(t_2) \propto S_{pp}^{\parallel}(t_2) + 2S_{pp}^{\perp}(t_2) \] (6.19)

If the optical pulses are not short compared to the dynamics of the system, the finite length of the pulses must be considered. Then, the nonlinear polarization has to be evaluated using Equs. 6.4 and 6.8 by convolving the nonlinear response function with the optical pulse temporal shape. In this case, the double quantum coherence pathways \( S_7 \) and \( S_8 \) (see Eq. 3.14 and Fig. 3.2) should also be considered. The impulsive limit has a great advantage, since it only requires propagation along two time variables (\( t_1 \) and \( t_3 \) for selected values of \( t_2 \) for the 2D spectra; \( t_2 \) and \( t_3 \) for PP), thus significantly reducing the computational cost compared to finite pulse length calculations. Approximate expressions for well separated pulses with finite bandwidth were derived recently \([192]\).

### 6.3.1 Computational Benchmarks

An all-numerical approach for calculations of the third order vibrational response was presented, therefore it is useful to assess the computational cost of the method. The most expensive part of the calculations is the propagation of doubly excited states. Diagonalizing the two particle Hamiltonian scales \( \sim M^6 \) and will only be feasible for \( M \leq 40 \). Using the split operator method, the propagation still scales \( \sim M^4 \), whereas all other operations scale either \( \sim M^2 \) (singly excited state propagation, doubly excited dipole interactions) or \( \sim M^3 \) (matrix multiplications in the singly excited basis). On the other hand, the signal calculation of a single trajectory already contains an ensemble average (\( \sim M \)), which results in a total scaling of the presented method as \( \sim M^3 \).
In the simulations of H$_2$O presented in Chap. 7 with $M = 128$, the doubly excited state propagation consumes $\approx 99\%$ of the calculation time. Good SNR was found when averaging $\approx 100$ trajectories per dipole orientation for pump and probe pulses. With 100 time steps in each time direction, a single trajectory calculation takes $\approx 2h$ on an AMD Athlon$^\circledR$ class processor, resulting in $\approx 1800h$ single processor computation time to gain a 2D spectrum in the impulsive limit.

Simulations on liquid formamide presented in Sec. 8.2.2 behave similarly. The reduction in computational cost due to the somewhat smaller system ($M = 98$) is compensated by the necessity of longer propagations along $t_1$ and $t_3$ (250 time steps), caused by the smaller spectral width of the transition. As a consequence, a single trajectory calculation is somewhat more costly than for H$_2$O ($4 - 6h$). However, due to reduced fluctuations in the molecular system only $\approx 50$ trajectories per dipole orientation were necessary for acceptable SNR. The resulting total computation time is then very similar to the H$_2$O case.

### 6.4 Interference Between Liouville Pathways in Excitonic Systems

In this section, interference effects as they appear in simulations of the nonlinear response of excitonic systems will be addressed, and how they affect the interpretation of the signal. It should be noted that these interferences are a purely theoretical phenomenon but may affect the total signal through numerical accuracy.

The third order response of a three band exciton model has three Liouville pathways - GSB, ESE and ESA - contributing to the total response along a given phase matching direction as shown in Fig. 6.1. For localized excitations these pathways can be analyzed and interpreted separately i.e. the GSB pathway can be written such that it reproduces the dynamics and spectral features of a bleached vibrational ground state. For excitons
this is not generally possible due to subtle interferences between the different pathways. Only the total signal as the sum of all pathways can be obtained. This phenomenon will be described and discussed in the following.

A collection of $N$ vibrational chromophores is considered, where the dipole moments are localized on each chromophore. The Green’s function expressions Eq. 6.6 are written in this local basis. For simplicity, the Condon approximation ($\mu_m(\tau) \equiv \mu$) shall be applied and only the rephasing GSB diagram $S_1$ will be analyzed:

$$S_1(t_1, t_3) = -\mu^4 \sum_{ijkl} \left( G_{ij}^{(1)}(\tau_4, \tau_3) \right)^\dagger G_{kl}^{(1)}(\tau_2, \tau_1)$$ \hspace{1cm} (6.20)

In the absence of vibrational coupling between these chromophores, i.e. localized excitations, $G^{(1)}$ is a diagonal matrix, and Eq. 6.20 simplifies even more.

$$S_1(t_1, t_3) = -\mu^4 \left( \sum_i G_{ii}^{(1)}(\tau_4, \tau_3) \right)^\dagger \left( \sum_k G_{kk}^{(1)}(\tau_2, \tau_1) \right)$$ \hspace{1cm} (6.21)

Eq. 6.21 can be interpreted as follows: if we think of the third order response as the correlation of coherences at different times, the two terms describe the coherences on modes $k$ and $i$ during $t_1$ and $t_3$, respectively. However, in Eq. 6.21 the sum does not only run over coherences of the same mode ($i = k$) but also over coherences between different modes ($i \neq k$). For illustration, Eq. 6.21 is recast:

$$S_1(t_1, t_3) = -\mu^4 \sum_i \left( G_{ii}^{(1)}(\tau_4, \tau_3) \right)^\dagger \left( G_{ii}^{(1)}(\tau_2, \tau_1) \right) -$$

$$-\mu^4 \sum_{i \neq k} \left( G_{ii}^{(1)}(\tau_4, \tau_3) \right)^\dagger \left( G_{kk}^{(1)}(\tau_2, \tau_1) \right)$$ \hspace{1cm} (6.22)
The first term resembles what is usually discussed as GSB. It locally measures the correlations between coherences during $t_1$ and $t_3$ and then performs an ensemble average ($\sum_i$). Double Fourier transforming this first term alone produces a 2D spectrum with one peak on the diagonal and a peak shape according to the spectral diffusion dynamics of the system, as illustrated in Fig. 6.2 (a).

The second term of Eq. 6.22 on the other hand, measures correlations between coherences of different modes $i$ and $k$. Even in the extreme case of a purely inhomogeneously broadened system, the 2D spectrum of this contribution alone would show a round shape (no stretching along the diagonal). An example is shown in Fig. 6.2 (b).

Figure 6.2: Double Fourier transform of the first (a) and second (b) term of Eq. 6.22. As an example, the $t_2 = 0$ fs, $\kappa = 12$ cm$^{-1}$ water data shown in Fig. 7.6 was used.

However, for localized excitations this second term does not produce a nonlinear signal. It can be shown straightforwardly that it is cancelled exactly with equivalent terms in $S_2$ and $S_3$. Thus, by only considering these diagonal contributions to the response the usual picture and interpretation of the GSB, ESE, and ESA can be recovered.

For excitons, it is not strictly possible to extract the individual contributions to the total response. The response can be written down and interpreted similarly to Eq. 6.22, now also taking into account the vibrational couplings resulting in nonzero off-diagonal elements of the Green’s functions:
\[
S_1(t_1, t_3) = -\mu^4 \sum_{ij} \left( G_{ij}^{(1)}(\tau_4, \tau_3) \right)^\dagger \left( G_{ij}^{(1)}(\tau_2, \tau_1) \right) - \\
-\mu^4 \sum_{i \neq k, j \neq l} \left( G_{ij}^{(1)}(\tau_4, \tau_3) \right)^\dagger \left( G_{kl}^{(1)}(\tau_2, \tau_1) \right).
\]

(6.23)

The first term of Eq. 6.23 still resembles a GSB like peak shape. The second term, however, does not cancel out exactly with the other diagrams \( S_2 \) and \( S_3 \) as soon as \( V \neq 0 \) or \( \mu \neq 0 \), i.e. in the case of any anharmonicity in the system. This effect occurs due to energy transfer in the \( S_3 \) diagram that essentially leads to redistribution of anharmonic effects. The nonlinear signal contribution emerging from these \textit{off-diagonal} terms is neither GSB, ESE, nor ESA. It only emerges as a subtle interference and incomplete cancellation between the diagrams.

In general, these off-diagonal contributions scale as \( N^4 \) since each dipole can act on a different chromophore. However, a nonlinear signal is generated only when all 4 interactions occur within the coherence size of the exciton. Otherwise the contributions cancel due to destructive interference between all pathways. This partial destructive interference prevents a simple interpretation of the signal in terms of the individual pathways [128].

It should be noted that the total signal will be significantly weaker than the individual diagrams depending on the ratio between the total system size and the coherence size of the excitons. This interference reflects the fact that individual pathways scale as \( N^4 \) whereas the overall response only scales as \( N^2 \). It should be done carefully since it may affect the numerical accuracy of simulations. The quasiparticle representation and the nonlinear exciton equations build this interference from the outset and avoid this difficulty [190, 193].
### 6.4.1 Ad hoc Population Relaxation

The phenomenon described in Sec. 6.4 has a direct impact on the ad hoc description of population relaxation for vibrational excitons. Population relaxation is included by adding relaxation factors $\Gamma$ to Eq. 6.8.

$$S_{I}(t_1,t_2,t_3) = \left( \sum_{k=1}^{3} S_k(t_1,t_2,t_3)\Gamma_k(t_1,t_2,t_3) \right)$$

$$S_{II}(t_1,t_2,t_3) = \left( \sum_{k=4}^{6} S_k(t_1,t_2,t_3)\Gamma_k(t_1,t_2,t_3) \right)$$

(6.24)

It is often assumed that the different levels of excitation have different decay times $[13, 90]$, i.e. $T_1$ for ground and excited state populations $|0\rangle\langle0|$ and $|1\rangle\langle1|$, $T_1/2$ for $|0\rangle\langle1|$ coherences, and $3T_1/2$ for $|1\rangle\langle2|$ coherences, as shown in Eq. 6.25.

$$\Gamma_{1,2,4,5}(t_1,t_2,t_3) = \exp\left(-\frac{-t_1 - 2t_2 - t_3}{2T_1}\right)$$

$$\Gamma_{3,6}(t_1,t_2,t_3) = \exp\left(-\frac{-t_1 - 2t_2 - 3t_3}{2T_1}\right)$$

(6.25)

No such procedure is possible when treating vibrational excitons. If different ad hoc factors as shown in Eq. 6.25 are applied to the different diagrams, the proper cancellation between the diagrams is prevented and the resulting nonlinear signal is physically wrong. Consequently, for excitons one can only use one relaxation factor for all the diagrams, e.g.

$$\Gamma_{1-6}(t_1,t_2,t_3) = \exp\left(-\frac{-t_1 - 2t_2 - t_3}{2T_1}\right).$$

(6.26)

This effect poses serious difficulties when trying to describe a persisting GSB as observed experimentally in the case of H$_2$O discussed in Sec. 7.4. Using a different $T_1$
time for the GSB diagrams $S_1$ and $S_4$ is not possible since this would prevent proper cancellation of the off-diagonal elements of the response (second term in Eq. 6.23), and thus lead to wrong results.

We instead propose an approximate description for the GSB, that is the first term in Eq. 6.23 only. This can be expressed by rewriting the rephasing nonlinear response $S_I$ as follows. We now again include intermolecular couplings and fluctuations of the transition dipole moments.

\[
S_I = -\sum_{ijkl} \left( \mu_i(\tau_3)G_{ij}^{(1)}(\tau_3,\tau_2)\mu_j(\tau_2) \right)^\dagger \left( \mu_k(\tau_1)G_{kl}^{(1)}(\tau_1,\tau_0)\mu_l(\tau_0) \right) \times \\
\times \exp\left(-\frac{t_1 - t_3}{2T_1}\right) \exp\left(-\frac{-t_2}{T_1}^{ijkl}\right) + \\
+ \left(S_2(t_1, t_2, t_3) + S_3(t_1, t_2, t_3) \right) \exp\left(-\frac{-t_1 - 2t_2 - t_3}{2T_1}\right)
\]

(6.27)

where we choose $T_1^{ijkl}$ as

\[
T_1^{ijkl} = \begin{cases} 
T_{1,GBS} & \text{for } i = k \text{ and } j = l \\
T_1 & \text{otherwise}.
\end{cases}
\]

(6.28)

The nonrephasing response $S_{II}$ is done equivalently. Here, $T_{1,GBS}$ is the lifetime of the GSB and $T_1$ is the excited state population lifetime. Using Equs. 6.27 and 6.28, we can now choose different times $T_{1,GBS}$ and $T_1$ without preventing the proper cancellation of the off-diagonal elements of the response, i.e. we can describe a ground state bleach that persists beyond the excited state population time $T_1$, by using a respectively larger value $T_{1,GBS}$. For the data shown in Fig. 7.7 we chose $T_1 = 200$ fs and $T_{1,GBS} = \infty$.

For illustration, we show the different contributions for the $t_2 = 0$ fs, $\kappa = 12 \text{ cm}^{-1} \text{ H}_2\text{O}$ data (see Chap. 7) in Fig. 6.3. The GSB contribution as discussed above is shown in (b). At $t_2 = 0$ fs, the ESE is identical to the GSB. It is therefore possible at this population
Figure 6.3: 2DIR correlation spectra of H$_2$O (see Chap. 7) at $t_2 = 0$ fs for $\kappa = 12$ cm$^{-1}$. (a) Full response, (b) GSB only, (c) ESA extracted from (a) and (b). All spectra are normalized to the full response amplitude. Note the scales for each spectrum.

Time only, to fully dissect the response into the different contributions. In Fig. 6.3 (c) we show the resulting ESA contribution. From the amplitudes of the signals we see that about 50% of the total amplitude is lost in the full response due to cancellation between the peaks. Similarly, the antidiagonal width of the peaks is significantly narrower in the full response compared to the individual contributions, greatly distorting simple analysis of the dynamics.
Chapter 7

Simulation of the 2DIR Spectrum of Liquid Water

This chapter presents the first and most important application of the protocol for simulating the nonlinear vibrational response of disordered fluctuating excitons described in the previous section. The 2DIR and PP response of the O-H stretch vibration in neat liquid water is calculated. This was the first work explicitly treating resonant vibrational coupling in the water nonlinear response modelling. It resolved some major discussions about the microscopic origin and the influence of vibrational coupling on the experimental 2DIR lineshapes, Chap. 5 [15, 142]. The results presented in this chapter were published recently [16].

7.1 Introduction

As discussed now extensively in this thesis, the special properties of liquid water ultimately originate from the correlations and intermolecular couplings in the extended hydrogen bond (H-bond) network [1, 2]. The fluctuating local electric fields and the variations in number, strength, and orientation of H-bonds strongly deform the potential energy surfaces. Coherent multidimensional spectroscopies [8–10] have most recently
become a valuable tool for the study of dynamics in such complex systems. As the optical equivalent of 2D NMR [30], both electronic and vibrational 2D coherent spectroscopies allow investigations of structural dynamics, coupling, dephasing, and relaxation mechanisms. So far, only a few 2D electronic spectroscopy studies have been reported [194–197]. Vibrational 2D spectroscopy on the other hand, usually referred to as 2D infrared (2DIR) spectroscopy, has been successfully used to study a wide range of systems, such as polypeptides [14, 84–90, 92], proteins [95–98] and DNA [198–200]. In particular the rapid structural dynamics in liquid water have been studied intensively by probing the ultrafast dynamics of the O-H stretching vibration [15, 18–25, 41, 46, 142]. Changes in the local environments are directly reflected in modulations of the transition frequencies, dipole moments, and anharmonicities of the stretching vibrations, making the O-H stretch mode the most direct probe of structural correlations and fluctuations in the liquid.

Most previous studies have focused on isotopically substituted systems HOD/D_2O and HOD/H_2O [22, 24, 25, 117, 121, 201] where the vibrational mode probed is localized on one bond of the molecule and no resonant vibrational energy transfer is observed due to large separation of the chromophores. Most recently, the first experimental studies on pure H_2O have shown significantly faster structural dynamics [15, 142] compared to the HOD systems. Stronger coupling to librational motions was found to be the main reason for this behavior, although some contribution from resonant energy transfer (ET) and delocalization of the vibrational excitations are also expected.

In general, the analysis of 2D spectra is complicated by the large line width of the transitions. The resulting overlap and interference between different peaks in the spectra often greatly distort the peak shapes, preventing simple extraction of the dynamic parameters of interest. The 2D spectra become even more convoluted in systems with pronounced intermode couplings which lead to delocalized excitations or formation of excitons. Some experimental approaches have been developed to amplify features of interest
and reduce complexity of the spectra [202, 203]. Still, high level theoretical modelling is required in order to reliably extract physical and chemical information from these data.

Initially, most 2D modelling approaches relied on the assumption of Gaussian statistics for transition frequency fluctuations of spatially localized vibrational or electronic modes. Then, the cumulant expansion can be truncated at 2nd order [7] and all non-linear spectroscopic observables are characterized by the frequency correlation function (FCF) $C(t) = \langle \delta \omega(t) \delta \omega(0) \rangle$. The FCF is usually obtained from molecular dynamics (MD) with various strategies for mapping the MD observables, e.g. electric fields, onto the transition frequencies [91, 92, 117–119]. This method was extended to include bath modulation of the transition dipole moments (non-Condon effects) [121]. In some special cases, approximate descriptions can be found to describe non-Gaussian statistics of the transition frequency fluctuations [14].

Several methods have been developed to treat intermode coupling leading to energy transfer [92], chemical exchange [204], and formation of excitons [111, 190, 200]. As long as the charge densities of the coupled states do not overlap, the delocalized states can be described as Frenkel excitons [123]. When the site frequency fluctuations are small compared to the intermode couplings, one can describe the system in a fixed exciton basis, with a pertubative description of the energy transfer between exciton states [118, 123]. If the fluctuations and couplings are comparable, exciton transport is a non-adiabatic process and multiple state crossing prevents the use of that basis [90].

Numerical integration of the Schrödinger equation (NISE) [16, 92, 204] is well suited to describe such complex dynamics. The major drawback of the method has so far been the high computational cost since it required diagonalizing the two-particle Hamiltonian. For that reason, the method was limited to either linear response calculations or small systems. We have shown in Chap. 6 that by introducing the split-operator technique [16, 191] the computational cost of NISE can be dramatically reduced enabling this method to be applied to a wide range of molecular systems. The modelling approach
described in Chap. 6 is well suited to simulate the nonlinear vibrational response of liquid water. This is due to its capabilities, at least in principle, to reproduce the key features of the nonlinear response observed in the experiment [142]: frequency dependent spectral diffusion dynamics, frequency dependent anharmonicities, likely nonadiabatic and partially coherent energy transfer dynamics, i.e. exchange between fluctuating disordered vibrational excitons. In the following we show how we obtain the vibrational Hamiltonian for liquid water and that indeed the model does reproduce these key features convincingly.

7.2 The Effective Vibrational Hamiltonian

The vibrational Hamiltonian was constructed according to Sec. 6.1. Two fundamental modes per molecular site (symmetric and antisymmetric stretch) were assumed, as shown in Eq. 7.1. Here, $\hat{B}_{m,\nu}^\dagger$ and $\omega_{m,\nu}$ denote the creation operator and the fundamental transition frequency, respectively, for mode $\nu$ ($\nu = 2, 3$, symmetric, antisymmetric) at the molecular site $m$. The intermolecular couplings $J_{m\nu,m'\nu'}$ are calculated using dipole-dipole coupling as given in Eq. 7.2, where $\mu_{m,1\nu}$ are the fundamental transition dipole moments at molecular site $m$, $R_{mm'}$ is the distance between sites $m$ and $m'$, and $\tilde{R}_{mm'} = (X_m - X_{m'})/R_{mm'}$. Since the electrostatic map provides instantaneous local eigenstates, all intramolecular couplings are set to 0. This effectively means that all intermolecular motions are treated non-adiabatically while the intramolecular interactions are treated adiabatically.
\[ \hat{H}(\tau) = \sum_{m=1}^{64} \sum_{\nu=2}^{3} \omega_{m,\nu}(\tau) \hat{B}_{m,\nu}^\dagger \hat{B}_{m,\nu} + \sum_{m',m = 1}^{64} \sum_{\nu,\nu' = 2}^{3} J_{m\nu,m'\nu'}(\tau) \hat{B}_{m,\nu}^\dagger \hat{B}_{m',\nu'} + \]
\[ + \sum_{m,m',n,n'=1}^{64} \sum_{\nu,\nu',\gamma,\gamma' = 2}^{3} V_{m\nu,m'\nu',n\gamma,n'\gamma'}(\tau) \hat{B}_{m,\nu}^\dagger \hat{B}_{n,\gamma}^\dagger \hat{B}_{m',\nu'} \hat{B}_{n',\gamma'} \]  
\[ J_{m\nu,m'\nu'}(\tau) = \frac{1 - \delta_{mm'}}{4\pi \varepsilon} \times \]
\[ \times 3 \mu_{m,1\nu}(\tau) \cdot \hat{R}_{mm'}(\tau) \mu_{m',1\nu'}(\tau) \cdot \hat{R}_{mm'}(\tau) - \mu_{m,1\nu}(\tau) \cdot \mu_{m',1\nu'}(\tau) \]
\[ R_{mm'}^3(\tau) \]  

The intramolecular anharmonicities \( V \) with \( m = m' = n = n' \) are calculated as the difference between the overtone frequencies provided by the electrostatic map (see Sec. 7.3) and the respective harmonic values. For example, the anharmonicity shift of the antisymmetric overtone on molecule \( m=1 \) is \( V_{1313,1313} = \omega_{1,5} - 2\omega_{1,3} \). The distributions of the intramolecular anharmonicities are shown in Fig. 7.1. We also treat intermolecular anharmonicities, or coupling anharmonicities, that arise from anharmonic transition dipole moments (see below, Eq. 7.3), affecting the dipole-dipole coupling between local overtones and intermolecular combination bands. Still, the anharmonicity matrix \( V \) is rather sparse, greatly reducing the computational effort.

Figure 7.1: Diagonal O-H frequency anharmonicities. (a) Symmetric overtone \( \omega_4 \), (b) antisymmetric overtone \( \omega_5 \), and (c) intramolecular combination band \( \omega_6 \), plotted as histograms versus their respective fundamental frequencies.
In a similar way, the transition dipole operator is constructed using Eq. 6.3 modified to account for the two fundamental modes per molecule, as shown in Eq. 7.3.

\[
\hat{\mu}(\tau) = \sum_{m=1}^{64} \sum_{\nu=2}^{3} \mu_{m,1\nu}(\tau) (\hat{B}_{m,\nu}^\dagger + \hat{B}_{m,\nu})
\]

\[
+ \sum_{m=1}^{64} \sum_{\nu'\nu''=2}^{3} \Delta \mu_{m,\nu\nu'}(\tau) \left( \hat{B}_{m,\nu'}^\dagger \hat{B}_{m,\nu'}^\dagger \hat{B}_{m,\nu} + \hat{B}_{m,\nu'} \hat{B}_{m,\nu'}^\dagger \hat{B}_{m,\nu}^\dagger \hat{B}_{m,\nu'} \right)
\]  

(7.3)

Here, \(\mu_{m,1\nu}\) are the fundamental transition dipole moments for mode \(m\) (transition from ground state into symmetric/antisymmetric fundamental mode \(\nu = 2, 3\)) at molecular site \(m\). The distributions of amplitudes for fundamental transition dipole moments are shown in Fig. 7.2 as a function of the respective fundamental transition frequencies.

In Eq. 7.3, we neglected intermolecular anharmonicities of the transition dipole moments. The intramolecular anharmonicities are calculated as the differences between the transition dipole moments involving overtones (\(\mu_{m,\nu\nu'}, \nu = 2, 3, \nu' = 4, 5, 6\)) and their harmonic counterparts. This is particularly important for harmonically forbidden transitions \(\mu_{m,25}\) and \(\mu_{m,34}\), which are now enabled due to the anharmonicities.

Figure 7.2: Histograms of the fundamental transition dipole moment amplitudes as function of the respective transition frequencies. (a) Symmetric mode \(\nu = 2\), (b) Antisymmetric mode \(\nu = 3\).
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7.3 Ab Initio Electrostatic Map

The electrostatic potential in the vicinity of a single H$_2$O molecule generated by the surrounding molecules is expanded to 2nd order in Cartesian coordinates (Fig. 7.3)

\[ U(\mathbf{X}) = U_0 - \sum_\alpha E_\alpha X_\alpha - \frac{1}{2} \sum_{\alpha,\beta} E_{\alpha\beta} X_\alpha X_\beta. \]  

(7.4)

Apart from the overall shift $U_0$, Eq. 7.4 has 9 independent multipole coefficient parameters (note that $E_{\alpha\beta} = E_{\beta\alpha}$). They were arranged in a vector

\[ \mathbf{C} = (E_x, E_y, E_z, E_{xx}, E_{yy}, E_{zz}, E_{xy}, E_{xz}, E_{yz}). \]  

(7.5)

\[ \mathbf{C} \] was calculated analytically at the origin of the molecular frame coordinate system from the surrounding water partial charges of MD configurations.

The anharmonic gas phase vibrational potential surface of H$_2$O in presence of the multipole field $\mathbf{C}$ is expanded in the three normal coordinates $Q_i$ to 6th order

\[ V(\mathbf{Q}; \mathbf{C}) = \sum_{k=1}^{6} f^{(k)}_{i_1\cdots i_k}(\mathbf{C}) \prod_{i=1}^{k} -Q_i. \]  

(7.6)

where $f^{(k)}_{i_1\cdots i_k}(\mathbf{C})$ are the anharmonic force constants, which are calculated by the quantum chemical calculations at the MP2/6-31+G(d,p) level using our modified Gaussian 03 code [117]. The Hamiltonian was expanded in a harmonic basis set and was recast into a normal ordered form [205]. The vibrational eigenstates are calculated by diagonalizing a Hamiltonian using the Implicit Restarted Arnoldi Method (IRAM) [205–207]. High energy basis states where the total number of excitations $n_T \equiv n_1 + n_2 + n_3$ are larger than 14 are neglected.
Table 7.1: Calculated anharmonic frequencies in the gas phase (is in cm$^{-1}$).

Molecular vibrational frequencies of the 6 Eigenstates (ground state, symmetric O-H stretch, antisymmetric O-H stretch, and their overtones and combinations) and the transition dipole moments between these states were parameterized with the multipole coefficients $C$.

The calculated gas phase frequencies of these 6 eigenstates are tabulated and compared with the reference high level calculation [208] in Table 7.1. The calculated frequencies are 0.6 % to 1.2 % higher than the reference calculations which employed higher computational level with larger basis sets. The anharmonicities of symmetric and antisymmetric O-H stretches have good agreement with the reference calculations (103 vs 113 cm$^{-1}$ and 71 vs 113 cm$^{-1}$).

The vibrational transition frequency from the ground state to state $\nu$ and the transition dipole moments between states $\nu$ and $\nu'$ were parameterized using the multipole coefficient vector $C$.

$$
\omega_{\nu} = \Omega_{\nu}^{\text{gas}} + \sum_{\alpha} \Omega_{\alpha}^{\nu} E_{\alpha} + \frac{1}{2} \sum_{\alpha\beta} \Omega_{\alpha,\beta}^{\nu} E_{\alpha} E_{\beta},
$$

$$
\mu_{\nu\nu'} = M_{\nu\nu'}^{\text{gas}} + \sum_{\alpha} M_{\alpha}^{\nu\nu'} E_{\alpha} + \frac{1}{2} \sum_{\alpha\beta} M_{\alpha,\beta}^{\nu\nu'} E_{\alpha} E_{\beta}.
$$

(7.7)

Here $\alpha$ and $\beta$ denote the 9 independent Cartesian coefficients $\alpha, \beta = x, y, z, xx, yy, zz, xy, xz, yz$ of the multipole vector in the molecular frame coordinate system.

The expansion coefficients are calculated by using the central difference formulas [205]. The calculated map is given in Table 7.2. Due to the molecular symmetry, the
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Table 7.2: Electrostatic ab initio map of the frequencies of the 6 states. The state $(n, m)$ represent the $n$ and $m$ quanta on symmetric O-H stretch and antisymmetric O-H stretch modes. Unit is in cm$^{-1}$ for $\Omega_{\text{gas}}$ and cm$^{-1}$ a.u.$^{-1}$ for $\Omega_{\alpha}^{(1)}$. 
Table 7.3: Electrostatic ab initio map of the allowed transition dipole moments of the 6 states (linear part). The state \((n_1, n_2) \rightarrow (m_1, m_2)\) represents the transition between the state \((n_1, n_2)\) and \((m_1, m_2)\). The \(x\) components of the transition dipole moments are always zero and \(y\) and \(z\) components are shown. Unit is in a.u. for \(M_{\text{gas}}\) and \(M_{\text{a}}^{(1)}\).

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In order to construct the vibrational Hamiltonian, we performed a molecular dynamics (MD) simulation of a small \((M = 64\) molecules\) Simple Point Charge Extended (SPC/E) water system at room temperature and constant volume using the GROMACS-3.3.1 program [209]. The electric fields generated by the solvent environment were calculated analytically [117] at every molecular site and time step. The electrostatic map described in the previous section was applied to calculate the transition frequencies and dipole moments for each molecule and time step.

Comparing the resulting distributions of the fundamental transition frequencies \(\omega_2\) and \(\omega_3\) to the experimental absorption spectrum, we found the solvent shifts generated by the electrostatic map insufficient. We compensated for this effect by scaling all electric fields with a factor 2.2 to match the maximum of the fundamental frequency distribution to the maximum of the linear spectrum of \(\text{H}_2\text{O}\), as shown in Fig. 7.4 (a). This scaling is likely necessary because of the purely electrostatic treatment of the interactions. High first derivatives with respect to the components \(E_x, E_y, E_{xy}, E_{xz}\) are 0. The electric field in parallel to the molecular axis \((E_z)\) blueshifts both symmetric and anti-symmetric O-H stretch frequencies since the negative charged oxygen moves toward the center of the hydrogens resulting in shorter O-H distances. The calculated map of the transition dipole moments is given in Table 7.3.
level quantum chemistry calculations of the H-bond interactions predict significant red shift due to H-bond cooperativity and through H-bond couplings \[81\]. The scaling is however believed to still capture the major dynamics of the local structures. In Fig. 7.4 (b) we show the resulting overtone frequency distributions.

Most recently, a similar ab initio map for the O-H stretching mode in HOD and H\(_2\)O was developed by the Skinner group \[119, 210\]. This work uses a local OH bond basis (opposed to the molecular Eigenstate basis used here), and can therefore treat nonadiabatic evolution of the intramolecular states and intramolecular energy transfer. Additionally, the electrostatic map is created by correlating the electric field along the OH-bond to the various quantum OH properties calculated from many small water clusters. This is expected to fully capture the charge transfer and exchange effects\[210\] of the hydrogen-bonding interactions that our above approach likely misses in the purely electrostatic treatment. In a recent review \[211\], they additionally suggest that the use of the electric field components \(\mathbf{C}\) at the center of charge might not be a good collective coordinate for the OH quantum motions. Likely a combination of these effects is responsible for the necessity for our empirical scaling. Calculations of the nonlinear vibrational response using the local mode basis are currently underway \[212\], and will provide a good benchmark for the quality of our combined ab initio/empirical electrostatic map approach.

### 7.4 Nonlinear Infrared Response

The main focus of this study is the effect of intermolecular coupling on the vibrational response when entering the fully resonant coupling regime for pure H\(_2\)O. We used the dielectric constant \(\epsilon\) as a scaling factor in the resonant dipole-dipole coupling Eq. 7.2 to reproduce the PA decay regime of \(\approx 80 \text{ fs}\) observed in H\(_2\)O \[15, 142, 174\]. Statistical analysis of the intermolecular coupling for a given value of the dielectric constant allows extraction of the average next neighbor coupling strength \(\kappa = \langle |J_{mm'}| \rangle\) for \(R_{mm'} < 3.2\)
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Figure 7.4: (a) Fundamental frequency distribution of the symmetric $\omega_2$ (black), antisymmetric $\omega_3$ (red) O-H stretching vibration, and combined symmetric and antisymmetric frequency distribution (green), blue: experimental linear spectrum [136]. (b) Overtone frequency distributions, symmetric overtone $\omega_4$ (black), antisymmetric overtone $\omega_5$ (red) and combination band $\omega_6$ (green).

\[ \hat{A}, \text{ where } R_{mm'} \text{ is the distance between molecules for the local modes } m \text{ and } m'. \]

Figure 7.5: Spectrally integrated signals. (a) PP transients for parallel (ppol) and crossed (xpol) polarization of pump and probe pulses for two coupling regimes. Figure 7.5 (b) and (c) show $S_{PA}$ and $S_{MA}$ calculated from these signals, respectively. Also shown in (b) is the experimentally observed PA in H$_2$O [142]. (c) $S_{MA}$ calculated from (a).

In Figure 7.5 (a), we show the spectrally integrated PP signal for parallel and crossed polarization of pump and probe pulses for two coupling regimes. Figure 7.5 (b) and (c) show $S_{PA}$ and $S_{MA}$ calculated from these signals, respectively. Also shown in (b) is the experimentally observed PA in H$_2$O [142].

For the uncoupled system, all dynamics observed in Fig. 7.5 are caused by bath
modulations of the transition dipole moments, i.e. dynamical non-Condon effects [121], since all energy transfer pathways are blocked and all populations remain constant. The PA reflects orientational modulations of the transition dipole moments which are caused by two major effects - (i) fluctuations of the transition dipole moments and (ii) librational motion and rotational diffusion. The former is found to be very strong in H$_2$O, accounting for $\approx 1/2$ of the signal decay. On the other hand, the $S_{MA}$ signal shows a fast initial decay that is entirely due to amplitude fluctuations of the transition dipole moments. This effect has not been addressed before, and we note that it should be considered when population relaxation dynamics are extracted from MA data.

When adding the intermolecular coupling, the anisotropy decay Fig. 7.5 (b) speeds up with increasing coupling strength and the long-lived components vanish. This effect can be clearly assigned to intermolecular energy transfer. We expect that the transfer process is at least partially coherent, and has to be understood as randomized energy transport between the disordered excitons. Since the total exciton population remains unchanged, the $S_{MA}$ signal is unaffected by these processes, as can be seen in Fig. 7.5 (c).

In Fig. 7.6, we show a series of 2DIR correlation spectra for two coupling regimes, uncoupled and $\kappa = 12 \text{ cm}^{-1}$, for different population times $t_2$. All spectra exhibit two peaks. The positive peak on the diagonal corresponds to the fundamental $0\rightarrow 1$ transition. The negative peak originating from $1\rightarrow 2$ ESA is red shifted due to anharmonicities. Strong interference between these two peaks results in significant signal cancellation and distortion of the peak shapes in the overlap region. Despite these distortions, we observe a clear V-shape of the ESA peak that in part is caused by the distributions of diagonal anharmonicities as shown in Fig. 7.1.

In both coupling regimes, the fundamental peak is stretched along the diagonal at population time $t_2 = 0 \text{ fs}$, indicative of initial inhomogeneity in the sample. This inhomogeneity is lost as with $t_2$ on very similar time scales for both systems. However, no
Figure 7.6: Simulated 2DIR correlation spectra of the O-H stretching vibration in H$_2$O for population times $t_2 = 0, 50, 100, 200, 500$ fs. Top panel: uncoupled system, bottom panel: $\kappa = 12$ cm$^{-1}$. Each spectrum is normalized to its maximum.

single time scale for loss of correlations can be extracted from these spectra. We instead observe these dynamics to vary across the spectrum. For both regimes, the red side loses correlations faster than the blue side. For the uncoupled system, we observe mainly two spectral components showing different dynamics which we attribute to the symmetric stretch on the red side and the antisymmetric O-H stretch on the blue side. Extraction of the respective time scales is however difficult due to the spectral overlap of the two modes. For $\kappa = 12$ cm$^{-1}$, no such separation is observed. The excitonic energy transfer instead smoothes out the dynamics across the spectrum. This is most obvious from the bending of the fundamental peak shape and the nodal line between the peaks in the $t_2 = 100$ and $200$ fs spectra.

For direct comparison with experiment, we corrected our simulation results for $\kappa = 12$ cm$^{-1}$ to match the experimental conditions by multiplication of the frequency domain response with the experimental excitation pulse spectra along $\omega_1$ and $\omega_3$. Additionally, we included population relaxation effects using an ad hoc description of the population relaxation with a population lifetime of $T_1 = 200$ fs [15]. We also model the persisting GSB observed in the experiment [142]. The extraction of the GSB contribution from the
total nonlinear response is, however, difficult for excitonic systems. This is discussed in Sec. 6.4. We instead use an approximate description for the GSB contribution presented in Sec. 6.4.1. With these assumptions, we find close agreement between our simulations and experiment as is shown in Fig. 7.7. In particular the tilt angle from the diagonal in the fundamental peak contours is very well reproduced.

Figure 7.7: 2DIR correlation spectra of the O-H stretching vibration in H$_2$O for population times $t_2 = 0, 50, 100, 200$ fs. Top panel: experimental data [142], bottom panel: $\kappa = 12$ cm$^{-1}$ corrected for experimental pulse spectrum and ad hoc population relaxation, see text. Each spectrum is normalized to its maximum. Figure adapted from Reference 1.

7.5 Discussion of the Nonlinear Vibrational Response of H$_2$O

The features and dynamics observed in the nonlinear vibrational response of neat H$_2$O can be assigned to two major contributions - local intramolecular effects and excitonic effects. The former are caused by the local 2D O-H stretching potential. Fluctuations in the local environment lead to modulations of the mixing between the states result-
ing in strong fluctuations of the fundamental dipole moments as well as the overtone frequencies and dipole moments. This can to some extent be interpreted as intramolecular energy transfer. Also, the strong local anharmonicities lead to breakdown of the harmonic selection rules, enabling additional pathways contributing to the nonlinear response. Additionally, we observe faster fluctuations for the symmetric stretch mode on the red side of the spectrum, see Fig. 7.6, compared to the antisymmetric mode on the blue side. Very similar effects have been observed for water in acetonitrile [17, 213], where this is attributed to non-Gaussian dynamics caused by local mode couplings. Similarly, modulations of the Fermi resonance of the symmetric mode with the HOH bending mode overtone is likely to impact the fast fluctuation time scales observed. This is included in our model through the quantum chemical calculations leading to the electrostatic map.

Apart from these dynamical effects, the distributions of transition frequencies and dipole moments and their anharmonicities also have significant impact on the peak shapes observed in the 2DIR correlation spectra. The dipole moment distributions as shown in Fig. 7.2 lead to amplitude distortion. The distributions of local frequency anharmonicities (see Fig. 7.1) create a distinct ESA peak shape and also lead to significant cancellation in the peak overlap region, see Fig. 6.3. The combination of all these effects makes it quite clear why a simple analysis of the spectra [42, 214], e.g. nodal line slope or dynamic line width analysis is likely to fail for H$_2$O, even for the uncoupled system.

The intermolecular coupling, on the other hand, mainly affects the PA dynamics. Here, the fast transfer time scales observed experimentally are reproduced for an average next neighbor coupling as small as 12 cm$^{-1}$. We find that the large number of acceptor modes, as well as anharmonicities and fluctuations in the system open up many intermolecular transfer pathways, leading to a full decay of the PA on these fast time scales, even for these small couplings. It is not possible to estimate the coherence contributions to the energy transfer process from our simulations. No clear physical model of energy transfer and dynamic delocalization for such fluctuating disordered excitons has been
Excitonic effects on the 2DIR correlation spectra are rather subtle. The overall dynamics are almost unaffected by the excitonic coupling. Rather than speeding up dynamics as one might expect, the excitonic interactions smooth out the fluctuations across the spectrum leading to a continuous distribution of spectral diffusion time scales from $\approx 100$ fs on the red side to $>200$ fs on the blue side of the spectrum. These time scales are in close agreement with experimental results [142], providing theoretical backup for the conclusions drawn there that the spectral diffusion at room temperature is dominated by librational motions despite spatial averaging by the excitations by resonant energy transfer. This is a very important fundamental point discovered in this thesis work.

We show here that indeed a very high level of theory is necessary to satisfactorily model the nonlinear vibrational response of the O-H stretching vibration of liquid H$_2$O. Non-Gaussian distributions and dynamics, non-Condon effects, distributions of anharmonicities, and excitonic interactions all significantly affect the signal, and therefore must be accounted for. The NISE approach combined with our split operator technique provides all this functionality at manageable computational cost, and in its generality is highly adaptable to any excitonic system.

### 7.6 Summary

Simulations of the two-dimensional infrared and pump probe response of the O-H stretch vibration in liquid water were presented. This was the first theoretical work explicitly treating intermolecular vibrational couplings and non-adiabatic effects to the nonlinear vibrational response. These simulations were possible through the new protocol using numerical integration of the Schrödinger equation with the split operator technique presented in Chap. 6.

Overall, the simulation results are in good agreement with the experimental data.
Chapter 7. Simulation of the 2DIR Spectrum of Liquid Water

[142]. In particular, the simulations reproduce the key features of the nonlinear response observed experimentally: frequency dependent spectral diffusion dynamics, frequency dependent anharmonicities, likely nonadiabatic and partially coherent energy transfer dynamics, i.e., exchange between fluctuating disordered vibrational excitons.

An \textit{ab initio} electrostatic map for the O-H stretching vibrations in water was specifically developed for this work. From comparing the simulated 2DIR spectra of isolated and interacting vibrational O-H stretch chromophores, it is found that intramolecular effects owing to the extreme sensitivity of the two-dimensional O-H stretching potential are the major cause of the dynamics observed. The experimental energy transfer times are reproduced for surprisingly small intermolecular couplings.
Chapter 8

Vibrational Excitons in Liquid Formamide

This work was performed in close collaboration with the group of R. Righini at the European Institute for Nonlinear Spectroscopy (LENS) in Florence, Italy. Experiments on the ultrafast spectroscopic properties of the amide I mode in liquid formamide were performed at LENS and published recently [66]. The contribution from this work is in analyzing and interpreting the 2DIR spectra of the vibrational amide I excitons in neat formamide by applying the simulation procedure developed for the study of liquid water, Chap. 6 and 7 [16, 135]. While some of the experimental results of Lima et al. [66] are reviewed here, the focus is on the simulation results and their interpretations. It is discussed how the evolution of the 2DIR spectra in this strongly excitonic vibrational system can be used to gain access to intermediate length scales of fast structural fluctuations and correlations in the H- network, information that cannot be accessed by any other method to date. The results presented in this chapter will be published shortly [215].
8.1 Introduction

From the previous discussion in this thesis, it can be well appreciated that coherent multidimensional spectroscopies [8–10] have emerged to be a very powerful tool in studying dynamics in complex systems. As discussed in preceding chapters, two-dimensional vibrational or infrared (2DIR) spectroscopy allows investigations of structural dynamics, intermolecular coupling, dephasing, and relaxation mechanisms in a wide range of molecular systems. Important applications pertain to the study of polypeptides [14, 81, 84–94], proteins [95–99, 216], DNA [198–200] and liquids [15, 16, 22–27, 66, 135, 142]. In this chapter, liquid formamide is explored as the simplest monomer unit that bridges liquid behavior to that of highly structured biomolecules.

In polypeptide and protein systems, structural changes are slow and the infrared lineshapes are often dominated by excitonic effects indicative of secondary or higher order structure [88, 91, 95, 199]. The evolution of the 2DIR spectra can then be used to track conformational changes on time scales of tens and hundreds of ps [84, 88]. For more site specific information, isotopic substitution is used [216]. In this case, the evolution of the 2DIR cross peaks can reveal the relative structural dynamics of labelled sites in strong analogy to 2D NMR studies. In liquids, an entirely different situation is often encountered. As discussed, most studies use isotopic substitution to eliminate any resonant interaction [22–27]. The 2DIR spectra are then sensitive to the most immediate structural environment. In these cases, it is the very fast, sub-ps dynamics of the local structure that dictates the 2DIR lineshapes and their evolution. In other words, the structural information gained from most 2DIR studies can be separated into two major regimes: (i) slow structural evolution on big length scales or (ii) fast structural dynamics on very short length scales.

In particular, for systems with extended H-bond networks, it would however be very interesting to also gain access to the dynamics on intermediate length scales. It is in these intermediate regimes that the true network characteristics become important. In the
usual protein vocabulary, this is the difference between primary and secondary or higher order structure. Only most recently, it was shown that the 2DIR spectrum of liquid water can be sensitive to intermediate length scales [142] through the delicate balance of local frequency fluctuations and intermolecular couplings [111]. At room temperature, the spectra are still dominated by local structural dynamics, corresponding to the primary structure in the protein language. At lower temperatures however, delocalization of the vibrational excitations becomes important and the 2DIR spectra report on the dynamics of structural correlations between 15-20 molecules [142], i.e. the secondary structure equivalent.

In this respect, liquid formamide (FA) is an ideal model system. The amide I vibrational oscillator is relatively insensitive to the local environment, electric field fluctuations and H-bonding. On the other hand, the resonant intermolecular couplings via transition dipole coupling (TDC) are comparable to those in water due to the large transition dipole moment. This results in largely delocalized excitons at ambient conditions [66, 83]. The dynamics of these delocalized states are dictated by the dynamics of spatial correlations in the H-bond network that modulate the excitonic states. It is in this sense that 2DIR can give a unique probe of the H-bond network dynamics in liquid FA.

Liquid FA forms an extended H-bond network and for that reason is often used as a model system for other H-bonded liquids such as water. However, it is now believed that the liquid structure, even though generally characterized by structural disorder, contains certain molecular aggregates and maintains some local structural properties of the crystalline phase [5, 58, 60, 62–66, 83]. The emerging picture exhibits mostly branched linear H-bonded FA chains with a minor appearance of ring-shaped oligomers and cyclic dimers [62, 64]. FA is therefore often considered a well-structured liquid [65, 66].

The importance of vibrational coupling between the local amide I modes in liquid FA was first discovered in polarized Raman experiments [60, 61]. In these measurements,
the difference in peak position between IR, isotropic and anisotropic Raman signals, the so-called Raman noncoincidence effect \cite{61, 83, 105-108}, is indicative of the resonant vibrational interactions and formation of vibrational excitons \cite{108}. Even though some understanding about prominent structural domains can be extracted, all these studies are limited to time-averaged properties of the FA liquid structure.

Here we investigate how by using 2DIR spectroscopy of the vibrational amide I excitons, the dynamics of the H-bond network spatial correlations on various length scales can be explored. The analysis is based on previous work \cite{66} where 2DIR pump probe spectroscopy and MD simulations of neat FA and a 1:10 $^{12}$C:$^{13}$C FA isotopic mixture were used to fully characterize the spectroscopic parameters of the amide I mode. The isotopic substitution allows to distinguish between the local frequency fluctuations and excitonic contributions to the linear and 2DIR lineshapes. The local structural dynamics were fully characterized in this study through appropriate modelling of the $^{12}$C FA impurity spectra. We now extend the modelling to also study and interpret the dynamics of the vibrational excitons in neat FA using the simulation procedure based on numerical integration of the Schröedinger equation (NISE) developed for the study of liquid water \cite{16, 135}. By correlating the spectral dynamics of the amide I excitons with microscopic structures of the excitonic modes, the possibilities of inferring the dynamics of the H-bond network are assessed.

## 8.2 Methods

### 8.2.1 Experimental Procedure

The experimental procedure was described in detail before \cite{66}. The 2DIR spectra were recorded in a spectral hole-burning pump probe setup. A Ti:Sapphire amplified laser system pumps two optical parametric amplifiers (OPAs) followed by difference frequency generation (DFG) in a Ag$_2$GaS crystal to generate broadband pump and probe pulses.
at $\lambda = 6 \mu m$ with a band width of $\sim 200 \text{ cm}^{-1}$. The pump pulse passes a Fabry-Perot filter reducing the pump band width to $15 \text{ cm}^{-1}$. In the hole burning experiment, the center wavelength of the pump pulse is scanned by adjusting the separation between the etalon mirrors. A wave plate in the pump beam allows switching between all parallel and crossed polarization of pump and probe pulses. The scanning-pump broadband-probe signal as a function of pump probe delay time and pump wave length is recorded spectrally dispersed using an imaging monochromator and a MCT detector array. The 2DIR spectra are generated by plotting the pump probe signal as a function of the pump (etalon) and probe (spectrometer) frequencies. The time and spectral resolution of these hole burning experiments is inherently limited through the use of an etalon. In the given experiments, the spectral resolution is $\Delta \nu = 15 \text{ cm}^{-1}$ and the temporal resolution is $\sim 0.7 \text{ ps}$.

8.2.2 Simulations of the Nonlinear Response

The nonlinear vibrational response of the amide I band in FA is calculated using the NISE method described in Chap. 6. The procedure is, in principle, identical to the calculations presented in Chap. 7: set up the vibrational Hamiltonian, determine the time-dependent Hamiltonian parameters and finally calculate the response. Whereas the final step is generic and identical between different vibrational systems, the first two steps are specific to the molecular system and vibration under study, and are described below.

Vibrational Hamiltonian and Empirical Electrostatic Map

A MD simulation of liquid formamide was carried out using the optimized potential for liquid simulation (OPLS) model by Jorgensen and Swenson [217]. The details of these simulations were described in detail before [66]. A 50-ps long, 2-fs time step trajectory of 96 FA molecules in a cubic box with periodic boundary conditions at room temperature was generated under constant volume, constant energy (NVE) conditions.
We employ an effective time-dependent amide I vibrational Hamiltonian in the local molecular basis with 4-fs time steps given in Eq. 8.1 which is derived from Eq. 6.2.

\[
\hat{H}_S(\tau) = \sum_m \omega_m(\tau) \hat{B}_m^\dagger \hat{B}_m + \sum_{m' \neq m} J_{m,m'}(\tau) \hat{B}_m^\dagger \hat{B}_{m'} - \sum_m \frac{\Delta}{2} \hat{B}_m^\dagger \hat{B}_{m} \hat{B}_m \hat{B}_m (8.1)
\]

Here, \(\omega_m(\tau)\) are the fundamental transition frequencies, \(\hat{B}_m^\dagger\) and \(\hat{B}_m\) are the creation and annihilation operators, respectively, of the amide I mode of molecule \(m\). The resonant vibrational couplings \(J_{m,m'}\) are calculated by transition dipole coupling (TDC), Eq. 7.2. Only a constant diagonal anharmonicity shift \(\Delta = 16 \text{ cm}^{-1}\) of the \(1 \rightarrow 2\) transition is considered.

Most commonly, the time-dependent Hamiltonian parameters such as transition frequencies, transition dipole moments and anharmonicities in Eq. 6.2 and 6.3 are acquired from electrostatic maps based on quantum chemistry calculations [91, 117–119, 135]. Here, we follow a much simpler approach using an empirical electrostatic map whose parameters are acquired by fitting the calculated linear spectra to the experiment. Despite this simplistic approach, we find excellent agreement with the experimental lineshapes. This is due to the special properties of the amide I band which is dominated by excitonic effects as a result of resonant vibrational coupling [66, 83], an effect that is well captured within our model. On the other hand, local electric field fluctuations have very little effect on the Hamiltonian parameters of the carbonyl stretching mode, compared to \(O-H\) and \(N-H\) stretching modes which are dominated by these electrostatics. As a consequence, the vibrational response of FA is quite insensitive to the local field fluctuations and the specifics of the electrostatic map.

The empirical electrostatic map assumes a linear Stark shift [218] of the transition frequencies with the electric field strength \(E_m^\mu(\tau)\) along the transition dipole moment direction [66]

\[
\omega_m(\tau) = \omega_0 + k E_m^\mu(\tau) \quad (8.2)
\]
where $k$ is the linear Stark coefficient and $\omega_0$ is a constant. The transition dipole operator is given by:

$$\hat{\mu}(\tau) = \mu_0 \sum_m e_m^\mu(\tau) \hat{B}^+_m + \hat{B}_m$$

with $\mu_0$ the constant amplitude of the transition dipole moments. The transition dipole moment is assumed to be fixed on each molecule $m$ along the gas phase direction $e_m^\mu(\tau)$: lying in the FA molecular plane tilted 20° from the C=O bond towards the C-N direction and fixed at the position indicated in Fig. 1 in the work of Torii and Tasumi [219]. The time dependence of $\hat{\mu}$ arises from orientational dynamics of the FA molecules extracted from the MD simulation. Thus, in Eq. 8.3 amplitude fluctuations and anharmonicities of the transition dipole moments are neglected.

The full map then effectively consists of 3 independent parameters to be determined empirically: the transition dipole amplitude $\mu_0$, the Stark coefficient $k$ and $\omega_0$. In order to acquire the map parameters, the linear response of two systems was calculated using the NISE formalism (Eq. 6.13) and the map parameters were optimized for a best fit to the experiment: (a, impurity) 10% $^{12}$C FA dissolved in $^{13}$C FA and (b, neat) neat $^{12}$C FA. These linear response calculations explicitly treat the non-adiabatic dynamics of the vibrational exciton system. We also included lifetime broadening effects through an ad hoc factor with a $T_1$ time of 1.4 ps as extracted from the broadband pump probe data [66]. As will be seen below, this is important especially for the impurity data where the lifetime broadening accounts for $\sim 12\%$ of the total line width.

First, $k$ and $\omega_0$ are fitted for the impurity system by assuming no resonant coupling ($J \equiv 0$ in Eq. 8.1). Since $\mu_0$ can only affect the IR lineshape through the TDC, the lineshape for (a) is independent of $\mu_0$. In fact, we found that the value of $k = 3168$ cm$^{-1}$ extracted by Lima et al. [66] from a model [220] based on the cumulant approximation of Gaussian fluctuations [7] also produces excellent agreement for the NISE simulations. The linear spectra of the impurity are shown in Fig. 8.1 in blue (NISE simulation with $k = 3168$ cm$^{-1}$) and green (experiment). This confirms the interpretation
of the amide I of the impurity system following Gaussian statistics represented by the FCF extracted from the MD simulations. In this picture, the value of $k$ directly leads to an amplitude of frequency fluctuations $\sqrt{C'(0)} = 12.4 \text{ cm}^{-1}$. With a full-width at half maximum (FWHM) of $\sim 25 \text{ cm}^{-1}$ for the frequency distribution and $\sim 18 \text{ cm}^{-1}$ for the linear spectrum, the effect of motional narrowing is evident. However, approximately 20% of the motional narrowing is compensated by $\sim 2 \text{ cm}^{-1}$ homogeneous broadening due to the finite lifetime of the transition.

![Figure 8.1: Experimental and simulated linear spectra of neat $^{12}$C FA (neat) and $^{12}$C FA dissolved in $^{13}$C FA (impurity). The electrostatic map parameters were fitted to the experiment, see text.](image)

Second, the transition dipole moment magnitude $\mu_0$ is determined by fitting the linear spectrum of excitonic vibrational spectrum Eq. 6.13 with intermolecular couplings to the experimental spectrum of neat $^{12}$C formamide, using the value of $k$ obtained from the impurity system. We find good agreement for $\mu_0 = 3.46 \frac{D}{A\sqrt{amu}}$ which is slightly larger than the value of $\mu_0 = 3.3 \frac{D}{A\sqrt{amu}}$ extracted from an all-static exciton basis analysis [66]. Both values are in good agreement with ab initio calculations [92]. As for the impurity system, motional narrowing is affecting the linear lineshape, which is compensated for
by a respectively larger value of the transition dipole moments. It is noteworthy that the motional narrowing effect of \( \sim 10\% \) is significantly weaker in the neat FA system (compared to the impurity system) due to the large excitonic broadening of the line width. The NISE approach is well-suited to analyze motional narrowing effects in linear spectra of excitons [92, 110].

The pronounced asymmetry of the excitonic lineshape with a tail into the high frequency region is natively reproduced in these simulations. The microscopic origin of the asymmetry is not entirely clear, but is certainly related to the coherence size and IR activity of the excitonic modes, as will be discussed in more detail below.

**Nonlinear Response Calculations**

The procedure for calculating the nonlinear response from a system of floating coupled vibrational oscillators using the NISE method with the split-operator approach was described in detail in Chap. 6 [135]. In short, the six relevant third order response functions are calculated in the local molecular basis through a series of dipole interactions and direct numerical propagations of the singly and doubly excited exciton manifolds. The split operator approach greatly reduces the computational effort of the doubly excited state propagations. The third order vibrational response was calculated in the impulsive limit.

**8.3 Results**

The two systems (impurity and neat FA, a and b) described in the previous section were analyzed. For comparison, the experimental and calculated 2DIR spectra for the impurity and the neat \(^{12}\)C FA system at population time \( t_2 = 0 \) fs are shown in Fig. 8.2. The simulated spectra were not corrected for the limited spectral and temporal resolution of the 2DIR PP experiments. The extraction of the impurity spectrum from the isotopic
mixture data was described elsewhere [66]. All spectra exhibit two peaks, the fundamental $0 \to 1$ transition on the diagonal and the red shifted excited state absorption (ESA) peak. All peaks are tilted and stretched along the diagonal, even though to different degrees, indicating initial inhomogeneity of the vibrational excitations. The reduced initial inhomogeneity of the experimental data is, in part, caused by the $\sim 0.7$-ps time resolution resulting in temporal integration over parts of the spectral diffusion dynamics. This effect is significant since in both systems the dynamics are comparable (impurity) or faster (neat) than this time resolution.

The 2DIR spectra of the impurity system, Fig. 8.2 (a) and (b), are well described by the FCF since the NISE results perfectly reproduce the dynamics and lineshapes predicted by the cumulant approximation of Gaussian fluctuations [66]. An overall correlation time of 900 fs is observed which corresponds to the correlation time extracted directly from the
FCF. The difference between the experimental and simulated 2D lineshapes originates solely from the resolution constraints of the 2DIR PP experiment.

Figure 8.3: Simulated 2DIR spectra of neat $^{12}$C formamide for different population times $t_2$. The blue side of the spectrum shows somewhat faster spectral diffusion dynamics ($\sim$200 fs) than the red side (300-400 fs). These differences are mostly washed out by $t_2=600$ fs.

For the excitonic, neat $^{12}$C FA system Fig. 8.2 (c) and (d), we also observe good agreement between the experimental and simulated 2DIR spectra - within the same resolution constraints. The line width and shapes are reproduced well, in particular the larger antidiagonal width on the blue side of the fundamental peak shape, indicating faster dynamics on this side of the spectrum. This feature is consistently observed in these experiments [66]. The apparent reduced initial inhomogeneity in the experimental spectrum is likely caused by faster spectral diffusion dynamics of the vibrational excitons compared to the impurity system. The experiment averages out the major part of these fast dynamics. This becomes obvious when investigating the evolution of the simulated
2DIR spectra with population time $t_2$, Fig. 8.3.

Spectral diffusion is monitored as the decay of the spectral inhomogeneity. Initially tilted and stretched peak shapes become vertical with increasing $t_2$. The overall spectral diffusion time scale is 200-400 fs, whereas indeed a somewhat faster loss of correlations is observed on the blue side of the spectrum ($\sim 200$ fs) compared to the red side of the spectrum (300-400 fs). These spectral differences are mostly washed out by 600 fs when most frequency correlation has decayed. With the harmonic dipole moment approximation Eq. 8.3, the peak amplitudes of fundamental and excited state absorption peaks are expected to be equal. Due to the asymmetry of the lineshapes, the decay of correlations also slightly changes the relative amplitudes of the two peaks as they partially cancel in the overlap region.

Figure 8.4: Simulated 2DIR spectra of neat $^{12}$C formamide for different population times $t_2$ for parallel (XXXX) and crossed (XXYY) polarization of pump and probe pulses. The crossed polarization spectra exhibit reduced inhomogeneity, with the feature on the blue side even more pronounced than for parallel polarization conditions.
It is interesting to compare the 2DIR spectra for different polarization conditions. For direct comparison, the 2DIR spectra for parallel (XXXX) and crossed (XXYY) polarization of the pump and probe pulses for different population times are shown in Fig. 8.4. A clear noncoincidence of the 2DIR lineshapes is observed between pairs of 2DIR spectra for each population time $t_2$. These differences are most pronounced at $t_2 = 0$ fs, and have mostly decayed by $t_2 = 600$ fs. The crossed polarized spectra (XXYY) generally exhibit an overall reduced inhomogeneity. The increased antidiagonal width on the blue side of the spectrum is even more pronounced than for the all parallel polarization. This 2DIR noncoincidence effect is likely closely related to the Raman noncoincidence effect observed in liquid formamide [61, 83].

In fact, the same trends for the change in 2DIR lineshape were also observed in the 2DIR PP experiment. In Fig. 8.5, we show the 2DIR spectra at population time $t_2 = 0$ fs for parallel and crossed polarization of pump and probe pulses. Data is shown for two different temperatures, 25°C and 2°C. At room temperature the difference between the two polarization conditions is rather subtle. This is mostly caused by the combination of fast spectral diffusion and limited time resolution of the experiment. Since most initial inhomogeneity is already lost to this effect in the all parallel XXXX spectrum, the further reduction of the inhomogeneity in the XXYY spectrum not very pronounced but still detectable. However, in the data for the lower temperature (bottom of Fig. 8.5) the effect is very clear. Here, the initial inhomogeneity for XXXX is stronger and, in consequence, the difference to the XXYY is obvious.

We suspect that the increased inhomogeneity at lower temperatures is related to a more stable structure with more extended H-bonded complexes close to the freezing point. The same effect was observed in the 2DIR spectrum of liquid water [142]. However, more experimental data is required, preferably with improved resolution, in order to safely address this point. A photon echo 2DIR setup for the mid-IR spectral region removing all the resolution constraints of the hole-burning experiments is currently being built.
Figure 8.5: Experimental 2DIR spectra of neat $^{12}$C formamide for parallel (XXXX) and crossed (XXYY) polarization of pump and probe pulses at two temperatures. As in the simulated spectra Fig. 8.4, the crossed polarization spectra show reduced inhomogeneity. The blue side of the spectrum generally has a broader antidiagonal width consistently for all spectra. The difference between XXXX and XXYY is more pronounced at lower temperature.

We want to further investigate the 2DIR lineshape differences between the parallel and crossed polarization conditions. The 2DIR difference spectra XXXX - XXYY (not shown) are too convoluted to be interpreted directly. Instead, we aim to evaluate if there is a spectral dependence to these differences, i.e. if they are stronger or weaker for certain parts of the spectrum. This is well captured by integrating the 2DIR difference spectra\footnote{The differences are taken after normalizing both XXXX and XXYY to their respective positive maximum value.} for $t_2 = 0$ along the detection axis $\omega_3$ and plotting the integral value as a function of the excitation frequency. To prevent cancellation between the positive and negative signal parts, the absolute squared values of the spectra are integrated. The resulting traces...
are shown in Fig. 8.6 for the simulated (a) and the experimental (b) room temperature results. To compare the integrated differences to the spectral profiles, the equivalent quantity ($\omega_3$ integration over the absolute squared value of the 2DIR spectrum) for the XXXX spectrum is also shown.

![Integrated 2DIR Difference Spectra](image)

Figure 8.6: Experimental (a) and simulated (b) integrated 2DIR difference spectra of neat $^{12}$C. The absolute squared values of the 2DIR XXXX-XXYY difference spectra were integrated along $\omega_3$ and are plotted as a function of $\omega_1$. To compare to the spectral line shapes, the equivalent integration for the XXXX 2DIR spectra is also shown. For both, simulation and experiment, the differences are concentrated on the blue side of the spectrum.

From Fig. 8.6 it is clear that the major differences between the 2DIR spectra for the two polarization conditions occur on the blue side of the spectrum, for both experimental and simulated spectra.

### 8.4 Discussion

The linear lineshape of the amide I vibration reports on excitonic mode structure in liquid formamide. It has been reported that the vibrational modes in liquid FA are delocalized over up to 60 molecules [66]. Some model liquid studies even predict excitonic states
extending over up to 120 molecules [111]. The common approach to characterize the delocalization size of disordered vibrational excitons is to evaluate the participation ratio 
\[ \eta = \left( \sum_k \phi_k^4 \right)^{-1}, \]
where \( \phi_k \) are the Eigenstate wave function coefficients in the molecular basis. The size of the vibrational excitons critically depends on the balance between local disorder of the molecular transition frequencies and the magnitude of the resonant vibrational couplings [111]. It is the insensitivity of the molecular amide I vibration to the local structure (small local frequency disorder) in combination with its large transition dipole moment (large vibrational couplings) that leads to these largely extended states. The specific normal mode structure, their IR and Raman activity, on the other hand is modulated by the relative geometrical arrangement of the molecular transition dipole moments involved in these modes. In that sense, the IR and Raman lineshapes are also sensitive to the microscopic structure in the liquid.

Such normal mode analysis is intrinsically static, neglecting the influence of structural dynamics on the properties of the delocalized state. It is expected that rapid fluctuations in the liquid structure will dynamically localize the excitonic wave functions. However, if these fluctuations are not too fast and their amplitudes not too large, the basic characteristics of the normal modes are likely still reflected in the properties of the fluctuating excitons. This picture is confirmed by the excellent agreement of the linear line shape, in particular the asymmetry thereof, calculated from normal mode approaches [66, 83]. As we find in this study, the effect of the structural dynamics on this lineshape through motional narrowing is well captured by small modifications to the intermolecular coupling strength. The static structure calculations generally underestimate these couplings. Modifications to the lineshape itself are small. Consequently, modulations to the local structure must be small during the inhomogeneous dephasing time of the amide I vibrations probed by the linear spectrum.

Extensive work was done by Torii and Tasumi [83, 108, 219] correlating the IR lineshape and the Raman noncoincidence effect with the special properties and correlations
in the microscopic structure of the liquid. The analysis is based on a combination of ab initio calculations of several FA clusters and careful analysis of coupling contributions from different pair interactions in liquid structures acquired from Monte-Carlo simulations. The most dominant species in the liquid structure are linear chains of trans-NH H-bonded molecules. These bonds are somewhat stronger than cis-NH H-Bonds \([5, 58]\) making the chains not only abundant but also stable. The strongest IR active modes originating from intra-chain couplings are in-phase motions (fundamental chain modes) with the mostly parallel transition dipole moments. The longer the chains, the lower the frequency of the most IR active modes \([81]\). These strongly IR active modes from chains are likely to produce the majority of the red side of the IR spectrum. Disorder within the chain both reduces the IR activity (lowering the parallelism of the transition dipoles) and increases the transition frequency through reduced couplings (TDC). Modes with lower IR activity (partial cancellation through out-of-phase oscillations) are generally higher in frequency \([81]\). Disorder also softens the IR activity selection rules, increasing the contributions from higher order modes. The effect of interchain interactions is unclear at this point.

Other structures in the liquid are much less abundant and generally produce modes contributing mostly to the central part and the blue side of the IR spectrum \([83]\). The important species here are trans-NH H-bonded ring-shaped oligomers, cis-NH H-bonded cyclic dimers, as well as non-hydrogen-bonded complexes. All these structures are characterized by a larger disorder as a result of weaker intermolecular interactions. Increased disorder is expected to generally create smaller exciton sizes. Additionally, the reduced parallelism of the transition dipoles involved reduces the IR activity of these modes.

It was proposed \([60]\) that two distinctly different species are responsible for the asymmetry and that the IR lineshape can be fitted with two respective sub peaks. Even though this oversimplified picture has been since discarded \([83]\), it is still likely that the different species described above can be distinguished. In the linear IR or Raman spectrum this
is, however, difficult since all the contributions are broadened by the various static and
dynamic disorder effects producing large spectral overlaps between the IR signatures of
the different species. Here, the 2DIR spectroscopy results can give additional insight.

In principle, the antidiagonal width of the 2DIR fundamental peaks at population
time $t_2 = 0$ and the evolution of the lineshapes with $t_2$ in Fig. 8.3 can have two different
origins for excitonic systems: (i) rapid fluctuations of the excitonic transition frequencies
and (ii) intermolecular energy transfer between different excitonic modes. The case (i)
is the standard spectral diffusion picture [7]. Within the cumulant approximation, the
fast components of the frequency correlation function broaden the $t_2 = 0$ antidiagonal
line width (motional narrowing limit) whereas the slower components can be observed as
the evolution of the 2DIR lineshape with $t_2$. For a Kubo type model [114] with only one
frequency correlation time, the $t_2 = 0$ lineshape and the evolution of the shape with $t_2$ are
intrinsically connected. Shorter correlation time simultaneously causes faster evolution
and larger initial antidiagonal width of the $t_2 = 0$ 2DIR line shape, and vice versa.

Case (ii) on the other hand is related only to coupling strength and the relative ar-
rangement of transition dipole moments. The 2DIR lineshape and its evolution is caused
by the emergence of coupling-induced off-diagonal cross peaks between the different vi-
brational modes. This effect is well known for spectrally well separated modes for instance
in polypeptide systems [89]. The initial ($t_2 = 0$) magnitude of the cross peak is related
to the spatial overlap of the excitonic wave functions (common ground state), and the
evolution reports on the vibrational coupling strength. The larger the coupling the faster
the cross peaks grow in. However, the cross peak intensity is also related to the relative
arrangement of the molecular transition dipole moments involved in the coupled states
[13, 125]. In the case of FA, the individual cross peaks cannot be resolved due to the con-
tinuous spectral distribution of interacting states. Statistically distributed cross peaks
would rather lead to an antidiagonal broadening of the peak shapes, much like the shapes
produced by fast spectral diffusion dynamics. The degree of broadening scales with cross
peak intensity distributions, which in turn are heavily affected by spatial overlap of the interacting states and the relative arrangement of the interacting transition dipoles. The $t_2$ evolution of the 2DIR line shapes, in this picture, relates to the coupling strengths. In principle, the initial cross peak structure as well as the evolution of the cross peaks can produce 2DIR lineshapes very similar to the situation of simple spectral diffusion of uncoupled chromophores.

Thus, two possible explanations for the increased antidiagonal line width on the blue side of the neat FA spectra exist: the excitonic modes on this side of the spectrum (i) fluctuate more rapidly or (ii) show increased coupling induced cross peak intensity, compared to the red side of the spectrum. Case (i) reports on structural dynamics leading to a picture of more rapidly fluctuating non-chain like structures. And indeed, this would not be surprising since these structures are generally characterized by weaker intermolecular interactions, further strengthening this interpretation. Case (ii) on the other hand would mainly report on increased static disorder and reduced parallelism of the interacting transition dipoles for excitons on this side of the spectrum.

The 2DIR spectra for different polarization conditions, Figs. 8.4 and 8.5, further strengthen the arguments for the importance of case (ii). It is well known that the off-diagonal cross peak amplitudes can be amplified using different polarization conditions, a method which simultaneously reduces the intensities of the diagonal peaks [202]. In fact, this effect is often actively used to eliminate strong diagonal peaks to better resolve cross peaks [94, 198, 199]. Even though the situation is again more complex in liquid FA due to the continuous, overlapping distributions of complex species, similar effects are expected in this case. From Fig. 8.6 it is clear that the dramatic changes of the 2DIR spectrum between polarization conditions occur on the blue side of the spectrum, i.e. there is a direct spectral correlation between the initial antidiagonal line width and the XXXX-XXYY 2DIR difference spectra. This strong correlation suggests that the 2DIR lineshapes are dominated by coupling induced cross peaks. In this case, the dynamics
of the 2DIR lineshape would only be related to the excitonic interactions (cross peaks growing in quickly) rather than to the structural dynamics in the liquid.

This interpretation is further supported by the time scales of 2DIR lineshape evolution reported in Fig. 8.4. The energy transfer times, measured by PP polarization anisotropy (not shown), are on the 200 fs (experiment) to 300 fs (simulations) time scale which is in good agreement with the overall dynamics of the 2DIR lineshape evolution, suggesting that indeed the 2DIR lineshapes are dominated by vibrational coupling effects. Even though the similarity of the time scales is intriguing, such direct correlation between observed spectral diffusion and energy transfer is not necessarily justified. In fact, in liquid water several different regimes of spectral diffusion-energy transfer time ratios have been observed [142]. In particular, 2DIR correlations decay slower than energy transfer times at low temperatures.

In order to address the issues of contribution of the structural dynamics to the 2DIR response, a simple test was performed. By artificially changing the speed of the MD simulation that is used to construct the Hamiltonian, we can speed up and slow down the structural dynamics and see what effect that produces in the 2DIR response. The same MD trajectory was used, but instead of extracting snapshots every 4fs, they were extracted every 2fs (slow) and every 8 fs (fast). Either way, the propagation steps in the nonlinear signal calculation was 4 fs, so this way we only manipulated (froze and melted) the structural dynamics with all other parameters unchanged. The 2DIR spectra were calculated for \( t_2=0 \) and 300 fs for XXXX and XXYY polarization conditions, to see the change on the initial 2DIR spectra and the evolution for both polarizations. All these 2DIR spectra are shown in Fig. 8.7. The different MD speeds are shown in the columns: slow - left, normal - middle, fast - right. The top two rows show the all parallel XXXX polarization condition, the bottom two rows show XXYY, for \( t_2=0 \) fs (rows 1 and 3) and \( t_2=300 \) fs (rows 2 and 4), respectively.

Overall, it is immediately obvious that the differences between the columns in Fig. 8.7
Figure 8.7: 2DIR spectra for slow (2 fs MD steps, left column), normal (4 fs MD steps, middle column) and fast (8 fs MD steps, right column) molecular dynamics. The spectra for XXXX (top two rows) and XYY (bottom two rows) polarization conditions are shown at $t_2=0$ fs (rows 1 and 3) and $t_2=300$ fs (rows 2 and 4).
are not very large for all spectra. This strengthens the previous arguments that the 2DIR spectra are mostly sensitive to the time-averaged structure, much more so than the dynamics. However, a number of small systematic changes is detectable. The overall spectral line width gets narrower from the left to the right due to an increased motional narrowing contribution. Again, this effect is not very big since the majority of the lineshape is due to excitonic effects. Secondly, the special feature on the blue side of the spectrum gets weaker with faster molecular dynamics. In the XXXX spectra, the feature is reduced in intensity, for the XXYY polarization condition the spectra simply get more symmetric with faster dynamics. This observation indicates that the asymmetry of the 2DIR lineshapes is dominated by local structure, while at least in the fast MD case in the right column, the structural dynamics average out these asymmetries. Thirdly, the lineshape change on the red side of the spectrum with the MD dynamics indicates some sensitivity to the dynamics. This is most obvious in the second row of Fig. 8.7, XXXX and $t_2=300$ fs. Here indeed a reduced frequency correlation for the faster MD case is observed in peak shapes that are more vertical, compared to the slower MD cases. However, the effects are rather subtle and it is questionable if experimental data will be able to distinguish these features within the present SNR.

A somewhat more quantitative result of the impact of structural fluctuations on the third order response can be acquired from photon echo peak shift (PEPS) measurements (see Sec. 3.2.4 for details). In the context of the simulation protocol in Chap. 6, the homodyne three pulse echo signal is acquired by $t_3$ integration of the abs-squared value of the photon echo response function:

$$
S^{PEPS}(t_1, t_2) = \int dt_3 |S^{k_i}(t_1, t_2, t_3)|^2
$$

(8.4)

In the peak shift measurement, the $t_1$ position of the maximum of $S^{PEPS}$ is plotted as a function of $t_2$. Due to the $t_3$ integration, all spectral information is lost in this analysis.
It does however provide a quantitative measure of the frequency inhomogeneity (initial PEPS value) as well as an overall time scale for the loss of frequency correlations. The PEPS data for the XXXX and XXYY polarization conditions of the slow, normal, and fast MD scenarios is shown in Fig. 8.8. The effect of slowing down and speeding up the MD speed is well captured in these plots. For all data points, the PEPS value is smaller for faster MD dynamics, indicative of faster spectral dynamics.

![Figure 8.8: Photon Echo Peak Shift data for XXXX (squares) and XXYY (circles) polarization for slow (red), normal (black), and fast (green) MD dynamics. A clear trend is visible with lower PEPS values for faster MD dynamics.](image)

The above discussion is indeed very interesting. However, more studies are required in order to quantitatively capture the complex interplay between structural disorder and fluctuations, intermolecular couplings and the 2DIR line shapes. With the available data, it is difficult to extract information on structural fluctuations on different length scales, case (i) above, directly from the 2DIR spectra. The coupling induced cross peak appearance and spectral diffusion are spectrally overlapping, competing effects. The 2DIR peak shapes seem dominated by the cross peaks, i.e. by time-averaged local structure. The photon echo peak shift measurement appears to be more sensitive to the structural dynamics in this particular scenario.
Experimentally, temperature dependent 2DIR studies with increased time and spectral resolution should help to isolate these effects since temperature is expected to change the delicate balance between structural fluctuations and medium range structural order while maintaining similar vibrational coupling strengths. It is expected, though, that temperature will also modulate the time-averaged local structural correlations. Alternatively, complementary information could be acquired from 2DIR measurements of other intramolecular modes in neat liquid formamide. The $N$-$H$ stretch motions are likely the most interesting candidate due to the strong modulations of the $N$-$H$ stretching potential from H-bonding. However, the $C$-$H$ stretch and the amide II motions might also be very interesting, and the full set of coherent vibrational dynamics should provide a clear picture of the liquid structure and dynamics.

### 8.5 Summary

Experimental and theoretical studies of the linear and the two-dimensional infrared spectra of the amide I vibrational mode in neat liquid formamide were presented. The strong resonant vibrational interactions between neighboring amide I modes lead to dynamic delocalization and formation of largely extended vibrational excitons. The nonlinear vibrational signals are simulated with a recently developed method employing direct numerical propagation with the split operator technique for efficient calculation of the nonlinear response functions of disordered fluctuating vibrational exciton systems. Both the linear and the two-dimensional spectra are dominated by the excitonic behavior rather than by local structure and structural fluctuations due to the insensitivity of the molecular amide I mode to local structure and the large transition dipole couplings.

The strong asymmetry in the linear and the two-dimensional spectra is attributed to different species in liquid structure, showing different behavior for trans-$N$-$H$ hydrogen-bonded linear chains on the red side of the spectrum and the various other molecular
complexes in the central and blue part. In the linear spectrum, the spectral signatures largely overlap due to distributions of disorder and IR activity that broaden the respective contributions. In the two-dimensional spectra and their population time evolution, a clear trend is visible with the blue side of the spectrum showing larger antidiagonal broadening and faster loss of correlations. This effect is even stronger comparing different polarization conditions.

Two different possible sources for the observed 2DIR lineshapes are discussed: different structural dynamics or cross peak appearance through different coupling conditions for the excitonic modes on either side of the spectrum. Even though both mechanisms contribute to the 2DIR signals, spectroscopic observations favor the coupling and cross peak appearance as the major source of the line shapes. Structural dynamics play a smaller role. This leads to the conclusion that the blue side of the spectrum is likely characterized by larger structural disorder and reduced parallelism of the molecular transition dipoles contributing to the respective excitonic states. Photon echo peak shift measurements appear to be more sensitive to structural dynamics than the 2DIR spectra in this particular system.
Chapter 9

General Discussion

The work of this thesis has focused on developing the necessary tools, experimental and theoretical, to study vibrational dynamics with 2DIR spectroscopy in neat H-bonded liquids. The motivation to pursue this problem is twofold: (i) being able to study the liquids in their native state to understand the microscopic mechanisms of structural fluctuations and correlations, vibrational energy redistribution and relaxation. This is essential to improve the general understanding of liquid dynamics, as well as the importance and details of the liquid-solute interactions in many biological systems. (ii) Using the resonant vibrational interactions in order to get additional information on structural correlations and dynamics on length scales probed by delocalized vibrational excitations. This approach is markedly different from the much more common studies with isotopically substituted and diluted systems which usually probe the most immediate structural environment. Up until now extremely few 2DIR studies of such neat liquids exist and this work has to be understood as a pioneering advance into this largely unexplored field. While the tools developed during this thesis allowed to resolve some important problems, certainly also a large number of new questions were created, many of which could not be fully addressed.

However, the technological challenges in being able to perform 2DIR studies of H-bonded liquids have been completely met. The development of the nanofluidic technology
described in Sec. 4.4 removed the last serious difficulty from these experiments. All other experimental problems had been previously satisfactorily solved within the Miller group and the 2DIR community. These experiments are now easily accessible and reliable, and a large number of experimental 2DIR studies will follow in the near future. The nanofluidic technology will likely also be widely used in closely related fields, such as transmission electron microscopy and ultrafast diffraction experiments of liquid samples, in the near future. This work manifests an important contribution to this technological advance.

Similarly, the improvement of 2DIR theoretical modelling through the split operator approach, Sec. 6.2.1, introduced in this work is significant. It removed the main difficulty in 2DIR modelling of vibrational excitons, that is the immense computational costs of previous approaches. Theoretical modelling of the 2D response of vibrational and electronic excitons in many different systems is now readily available at reasonable computational costs. In fact, the technique developed in this thesis is already being applied to protein and J-aggregate 2D studies [212].

This work has focused on two important problems: (i) the 2DIR spectrum of neat liquid water and how to understand the spectroscopic data in relation to structural dynamics and (ii) the properties of vibrational excitons in disordered H-bond networks in general and understanding the 2DIR response from these systems. Liquid formamide served as an excellent model system to study such excitations and provides a bridge to even more strongly correlated biomolecules like proteins.

9.1 The 2DIR Spectrum of Liquid Water

The 2DIR response of the O-H stretching vibration at ambient conditions is now well understood, based on the results presented in Chap. 5 and 7 and previous studies [15, 46].
The most important notion in comparison to previous studies using isotopic substitution is the highly resonant character of all the vibrational processes. Spectral diffusion, energy transfer, and population relaxation all happen on similar, extremely fast time scales, making the vibrational dynamics highly non-adiabatic. This is caused by the large anharmonicity of the H-bonded O-H stretching potential making it particularly sensitive to anharmonic bath motions. The two-dimensional character of the intramolecularly coupled O-H stretching potential adds to this sensitivity, since modulations of a single H-bond affect not only one O-H stretch but the mixing between two involved vibrations. Therefore, the spectroscopic observables in neat H$_2$O are much more sensitive to correlations in the H-bond network than in the case of isotopic substitutes. This explains the much faster spectral diffusion dynamics since the librational motions now play a more important role in modulations of the O-H stretching potential.

While the 2DIR response at ambient conditions is dominated by network correlations within the first solvation shell, the low temperature results extend the length scale of spatial correlations probed to $>15$ molecules. Surprisingly enough, this is only possible and intrinsically connected to a reduced modulation of the O-H stretching potentials through diminished librational motions in the liquid structure. Since the increased vibrational delocalization counters some of the reduced local fluctuations in the detected spectral diffusion dynamics, the marked change in the 2DIR response implies even more pronounced changes in the liquid dynamics. This was a very new result that had not been accessible by any other experimental techniques.

It should be noted, though, that the experimentalist has very little choice in what extent of spatial correlations is being probed by 2DIR in a particular sample. It is the intrinsic properties of the vibrational system, its anharmonicity, structural sensitivity and magnitude of resonant intermolecular interaction along with the underlying structural dynamics, that will dictate the spatial correlation length that can be probed. For larger molecules than water, one can potentially get different subsets of structural information
from probing the different vibrations in the molecule. However, the dynamic range of these studies will always be limited by the population lifetime and the appearance of thermally induced signals. In most cases, the relaxation times are interconnected with the other dynamic properties probed with 2DIR through the anharmonicity of the vibrational potentials.

The very idea of balancing incoherent and coherent measurements such as polarization anisotropy and 2DIR spectroscopy, respectively, in Chap. 5 in order to gain additional insight about the molecular systems holds many promises. This approach has been poorly used until now; in most cases the one-to-one correlation between spectral dynamics and structural fluctuations is assumed. Here it is shown that the 2DIR signals can be influenced by many factors and that conclusions on the structural dynamics should generally be drawn with much care. While these differences are still subtle in the case of liquid water, they are more pronounced for the amide I mode in liquid formamide, as discussed below.

Another important new insight into the dynamics of the O-H stretching dynamics was its frequency dependence, as discussed in Chap. 5 and 7. The fast spectral diffusion dynamics on the red side of the spectrum are likely a combination of two major effects. For one, increased hydrogen-bonding results in larger anharmonicity and stronger modulation of the transition frequencies on this side of the spectrum. Secondly, the fluctuating intramolecular coupling and resulting splitting between the two intramolecular states is likely to always cause faster fluctuations of the energetically lower lying state. This latter issue was addressed in Chap. 7 and in other recent work [17]. This is one example of how the specific properties of the vibrational Hamiltonian can affect the 2DIR signal beyond the mere structural dynamics in the liquid sample. These types of problems will likely occur more frequently in 2DIR in the near future, since more and more complex systems are being investigated, while the level of theoretical modelling has improved significantly over the last few years allowing to now address those issues.
9.2 2DIR Signals from Disordered Fluctuating Vibrational Excitons

One of the major problems addressed in this work is the understanding of how vibrational excitons can be used to study intermediate length scales of structural correlations and fluctuations. The possibility of such a dynamic probe of spatial correlations in the liquid structure can, in principle, be separated into two components: (i) the likelihood of vibrational exciton formation and (ii) the excitonic effects on the 2DIR response for a given vibrational system.

The former (i) is usually discussed in a framework using the delocalization size of the vibrational wave functions. If completely localized on a single molecular chromophore with all intermolecular interactions being either small or incoherent, we generally speak of localized states. If coherently delocalized over many molecules we speak of excitons. The extent of the exciton delocalization critically depends on the balance between local frequency disorder and the magnitude of the resonant intermolecular interactions. In such a static or normal mode picture, this analysis holds well and follows intuitive approaches. In liquids, the situations is more complex as a result of rapid fluctuations of the structure that lead to modulations of the local frequencies on the one hand and modulations of the excitonic wave functions and frequencies on the other hand. Multiple state crossing between many spatially overlapping exciton states makes their dynamics extremely complex. It would be helpful to be able to characterize these dynamic effects in an effective exciton size, but all attempts for such a classification during this work and in the 2DIR community have yet been unsuccessful. It was proposed that the respective general definition is irrelevant and the effective size is determined by the specific spectroscopic probe and only valid in this context [221]

Within the framework of the simulations presented in this thesis, the effective exciton size does not contribute since all signals are calculated in the molecular basis. As such,
the complex interference patterns that create the effective exciton size are intrinsically handled in these simulations. However, it is not possible to extract such information in the given model framework. Other studies have attempted to characterize fluctuating excitons, but in most cases the parameters determined only relate to incoherent energy transfer processes. For the sake of the discussion within this work, the normal mode picture is often applied. At least for systems with small fluctuations like formamide, this should still give an approximate description of the delocalized vibrational states. Hereby it is generally expected that the fluctuating excitons are smaller due to dynamic localization.

One important new aspect of disordered vibrational excitons was presented in Chap. 8: the influence of medium range structural order on the properties of the excitonic wave functions. The degree of geometrical medium range order not only affects the spatial extent of the excitonic wave functions but also influences the IR activity of the excitonic modes. In partially structured systems with many different structural species and generally largely extended excitons, the distribution of mode structures and IR activities is highly complex and will affect the spectroscopic observables, even for the linear response. For the case of liquid formamide, these distributions are difficult to disentangle and it would be interesting to design a model liquid system with an adjustable degree of structural order. This should help to better dissect the linear response and understand the IR mode structures of significance. Nonetheless, some basic structural trends were identified that will help to better understand the liquid structural dynamics.

No rigorous investigation of excitonic effects on the 2DIR spectra for dense disordered systems has been shown in the literature to date. The small set of systems studied in this thesis can however give some basic guidelines for future investigations. A few different regimes of excitonic effects on the 2DIR were encountered here, but this is very likely only a small subset of the possible scenarios.
The room temperature data and simulations of liquid water suggest minor impact of the excitonic character on the spectral diffusion dynamics observed in the 2DIR spectra. Here, the local fluctuations are so strong and rapid that they dominate the 2DIR response. The major change here appears in the switching from a vibration localized on one bond like in HOD in D$_2$O to the intramolecularly delocalized vibrational wave functions. The intermolecular effects play a minor role for the coherent dynamics probed in the 2DIR spectrum. They do, however, dominate the incoherent population dynamics.

At lower temperatures, the balance between fluctuations and couplings is shifted and the coherent motions of many water molecules contribute to the nonlinear vibrational signal. No theoretical scenario could be found that displays the same effect, in particular with spectral diffusion persisting beyond energy transfer times. It is suspected that the specific geometry of the relatively stable structural domains in liquid water near the freezing point are largely responsible for these observations. These highly specific molecular arrangements and dynamics in this near-phase transition point of the liquid are very difficult to reproduce in MD simulations and no reliable theoretical modelling of this situation could be developed here. Additionally, the strong structural modulation of the local vibrational potentials is likely to create "resonance channels" for the energy transfer along correlated structures in the liquid.

Finally, the 2DIR study of the amide I in liquid formamide revealed a significantly different scenario. Here, the small local fluctuations combined with the relatively large resonant couplings lead to very large excitons. Surprisingly enough, the results in Chap. 8 suggest very little sensitivity of the 2DIR spectra to structural dynamics. The spectra seem to be dominated energy transfer effects showing cross peak evolutions indicative of certain medium range structural anomalies. In this respect, the 2DIR spectra of this neat liquid behave much more like the response expected from rigid macromolecules such as proteins and DNA, where also the 2DIR spectra report on structure much more so than on structural dynamics. This conclusion was somewhat disappointing because it
was expected that the structural fluctuations on different length scales could be probed here. However, the presented results add an additional component to the existing results from linear techniques in order to better understand the complex liquid structure.

It would be very interesting to study more microscopic scenarios in order to develop an intuitive understanding of the 2DIR response of disordered vibrational excitons. Straightforward examples would be: different vibrational modes in liquid formamide (N-H stretch, C-H stretch, amide II), the bending mode in liquid water, the stretching and bending modes in water ice, methanol, ethanol, DMF, etc. Many of these systems have been studied by nonlinear vibrational spectroscopy but the coherent 2D measurements are still pending and would provide a more general basis for the understanding of disordered vibrational excitons.
Chapter 10

Conclusion

The structure and structural dynamics of neat hydrogen bonded liquids were studied experimentally and theoretically with coherent two-dimensional infrared (2DIR) spectroscopy. The study of neat liquids, instead of commonly used isotopic dilutions, adds additional components to the ultrafast vibrational response due to resonant intermolecular interactions between densely packed vibrational chromophores. The resonant interactions cause modification of the phase and population relaxation processes within the fully resonant hydrogen bond network, allowing these spectroscopies to study spatial correlations in the dynamics of the liquid structures.

New experimental and theoretical tools were developed during this work that significantly reduced the technical challenges of these studies, making them easily accessible for a wide range of systems in the future. A nanofluidic flow device was designed and manufactured that provides sub-micron thin, actively stabilized liquid sample layers wedged between also sub-micron thin windows. This development provides access to studies of nanometer-scale thick liquid samples not only with vibrational spectroscopy, but also with electron transmission and diffraction techniques and removes a major technical obstacle from these experiments. Further, a simulation protocol for nonlinear vibrational response calculations of disordered fluctuating vibrational excitons was developed that
allowed the first treatment of resonant intermolecular interactions in the 2DIR response of liquid water. This was due to the introduction of the split-operator technique that reduces the computational effort of these simulations by several orders of magnitude compared to previous approaches. The technique is very versatile and can be used for any vibrational or electronic system with excitonic effects.

The 2DIR spectrum of the O-H stretching vibration of neat liquid water was studied experimentally at different temperatures. The neat water vibrational response is characterized by the fully resonant interaction of all phase and population relaxation processes, all happening on a 100-fs time scale. At ambient conditions the loss of frequency correlations is extremely fast, faster than orientational and population relaxation of the vibrational excitation. With the help of the simulation study, these fast dynamics are attributed to very efficient modulations of the two-dimensional O-H stretching vibrational potential through librational motions in the hydrogen bond network, most sensitive to correlated hydrogen-bond motions in the first solvation shell. The spectral dynamics are found to depend on the overall distribution of hydrogen bond strengths across the spectrum. At temperatures near the freezing point, the librational motions, and thus the modulations of the O-H stretching vibrational potential, are significantly reduced. This leads to slowing down of spectral diffusion dynamics and coherent delocalization of the vibrational excitations. The comparison between intermolecular energy transfer times and frequency correlation times reveals significant spatial correlations over $\geq 15$ molecules in the low temperature liquid structure during the $\sim 200$-fs time scales probed by the 2DIR experiment.

The result provides the first proof of coherent delocalization of the vibrational excitations in liquid water. In this sense, this work establishes a fundamentally new view of vibrations in liquid water by providing a spatial correlation length involved in these excitations. In fact, this is the first time for the time-dependent frequency correlations
to be related to a correlation length scale in any liquid. It gives the a direct measure of correlated hydrogen-bond motions within the complex water network. As a result, it will be necessary to revise physical pictures that rely on fast local hydrogen bond fluctuations as the dominating terms the structural dynamics in water, and to consider significant contributions from the hydrogen-bond network interactions.

The structural regime of low temperature water studied in this thesis is expected to be comparable to the special situations of water confined to nanoscale volumes and in the proximity of biological molecules, which are generally characterized by slowing down of the structural dynamics. Especially for the biologically relevant scenarios, the water in the immediate proximity of the solute is expected to behave similar to the low-temperature pure water. This work shows that it will be crucial to consider correlated hydrogen-bond motions within the water network in facilitating extremely fast energy redistribution through the water solvent, and possible even water contributions to correlated biomolecule motions to fully understand this complex solute-solvent interplay.

The linear and 2DIR response of the amide I mode in neat liquid formamide is found to be dominated by very strong excitonic effects. Local frequency fluctuations are small compared to water, with similar resonant intermolecular couplings. This leads to largely extended vibrational excitons. The spectral response and dynamics are very sensitive to the excitonic mode structure and infrared activity distributions. The 2DIR lineshapes and their evolution are found to be dominated by energy transfer effects and, thus, are mostly sensitive to time-averaged medium range structural order in the liquid. The pronounced asymmetry of linear and 2DIR line shapes is attributed to structurally different species in the liquid characterized by their degree of medium range structural order. These results further support previous conclusions of formamide being a well-structured liquid.

This is a significantly different scenario from the liquid water case discussed above, where here the 2DIR response is essentially insensitive to correlated hydrogen-bond mo-
tions. Considering the well-structured character of formamide, such correlated motions are very likely. It is expected that probing the N-H stretching motions instead of the amide I mode would reveal these correlations. As the strong excitonic effects due to insensitivity of the local vibrational potential effectively average out fast hydrogen-bond motions, the 2DIR response then becomes sensitive to a different regime in the structure, i.e. relative arrangement of the formamide molecular transition dipoles on intermediate length scales. This exact structural domain is routinely probed with 2DIR from biological molecules like proteins. In this sense, liquid formamide constitutes an excellent transitional model system between disordered liquids and strongly structured biological molecules. As such, it will likely be studied in more detail in the future to test fundamental characteristics of strongly correlated hydrogen-bond motions as they occur in proteins.
Appendix A

Factorization of the Harmonic
Two-Particle Propagator

In the following, we will consider the harmonic part of the effective Hamiltonian denoted as $\hat{H}_0(\tau)$, i.e. the first two terms of Eq. 6.2:

$$\hat{H}_0(\tau) = \sum_m \omega_m(\tau) \hat{B}_m^\dagger \hat{B}_m + \sum_{m' \neq m} J_{m,m'}(\tau) \hat{B}_{m'}^\dagger \hat{B}_{m'}$$  \hspace{1cm} (A.1)

The infinitesimal propagators for singly excited states used in Eq. (6.9) are now denoted as $U_0^{(1)}$ written in the singly excited local basis $|m\rangle = \hat{B}_m^\dagger |0\rangle$:

$$U_{0,mn}^{(1)}(\tau) = \langle m | \hat{U}_0(\tau) | n \rangle = \langle m | \exp \left(-i \hat{H}_0(\tau) \Delta \tau \right) | n \rangle$$  \hspace{1cm} (A.2)

The doubly excited infinitesimal propagator $U_0^{(2)}(\tau)$ can be calculated by factorization of $U_0^{(1)}(\tau)$. In the following, we omit the explicit $\tau$ dependence for clarity.
\[ \begin{align*}
U_0^{(2)}_{mn,m'n'} &= \langle m, n|\hat{U}_0|m', n'\rangle \\
&= \delta_{mn}\delta_{m'n'}U^{(1)}_{0,mm'}U^{(1)}_{0,nn'} + \\
&\quad \sqrt{2}\left(\delta_{mm'}(1 - \delta_{m'n'})U^{(1)}_{mm'}U^{(1)}_{mn'} + \delta_{m'n'}(1 - \delta_{mn})U^{(1)}_{mm'}U^{(1)}_{nn'}\right) + \\
&\quad (1 - \delta_{mn})(1 - \delta_{m'n'}) \left( U^{(1)}_{mm'}U^{(1)}_{nn'} + U^{(1)}_{mm'}U^{(1)}_{nn'} \right), \quad (A.3)
\end{align*} \]

where \(|m, n\rangle = \frac{1}{\sqrt{1+\delta_{mn}}} \hat{B}^+_m \hat{B}^+_n |0\rangle\). This rather complicated structure of the two-particle propagator arises from the properties of the symmetrized two-particle basis. It can be shown straightforwardly that any basis transformation matrix in a symmetrized two-particle basis has the given structure.
Bibliography


[192] I. V. Schweigert and S. Mukamel. Simulating multidimensional optical wave-mixing 


[208] H. Partridge and D. W. Schwenke. The determination of an accurate isotope
dependent potential energy surface for water from extensive ab initio calculations

[209] H. J. C. Berendsen, D. van der Spoel, and R. van Drunen. GROMACS: A message-

[210] B. Auer, R. Kumar, J. R. Schmidt, and J. L. Skinner. Hydrogen bonding and
Raman, IR, and 2D-IR spectroscopy of dilute HOD in liquid D2O. *Proc. Natl.


[213] D. Cringus, T. l. C. Jansen, and M. S. Pshenichnikov. Heterogeneous Dynamics
of Coupled Vibrations. In E. Riedle, R. Schoenlein, P. Corkum, S. de Silestri,
York, 2009.

[214] K. Lazonder, M. S. Pshenichnikov, and D. A. Wiersma. Easy interpretation of

Probing the dynamics of spatial correlations in the hydrogen bond network of liquid

[216] J. Manor, P. Mukherjee, Y.-S. Lin, H. Leonov, J. L. Skinner, M. T. Zanni, and
I. T. Arkin. Gating Mechanism of the Influenza A M2 Channel Revealed by 1D


