Vibrational Dynamics of Aqueous Hydroxide Solutions
Studied using Ultrafast Infrared Spectroscopy

by

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Abstract:

Liquid water possesses an extended network of hydrogen bonds that is responsible for many of its interesting properties. Mobility of hydroxide ions in aqueous solutions is much higher compared to the ions of similar size and charge density. A proton can efficiently move from a neighboring water molecule to the hydroxide ion due to the presence of hydrogen bonds, resulting fast structural diffusion of the ion. On the other hand, this hydrogen bonding network of water undergoes fluctuations on femtoseconds to picoseconds timescale, influencing the intertwined hydroxide transport process. Studying the influence of water’s hydrogen bonding network on the proton transport process in aqueous hydroxide solutions is experimentally challenging, largely due to the lack of a suitable technique that is sensitive to the changes in the system on few tens of femtoseconds timescale. Vibrations in aqueous hydroxide solutions are sensitive to the strength of hydrogen bonding and hence vibrational frequencies, intensities and line shapes are closely associated with the structure and dynamics of the hydroxide ions. In this thesis, we have employed ultrafast infrared spectroscopy in conjunction with theoretical modeling to understand the nature of the vibrations and their dynamics in aqueous hydroxide solutions.

The infrared spectra of aqueous solutions of NaOH and other strong bases exhibit a broad continuum absorption for frequencies between 800 and 3500 cm\(^{-1}\), which is attributed to the strong interactions of the hydroxide ion with its solvating water molecules. This continuum absorption has limited distinguishable features whose molecular origin holds the key in explaining the vibrational dynamics. We have performed ultrafast transient absorption and 2DIR experiments on aqueous NaOH solutions, by exciting the O—H stretch vibrations and probing the response from 1350-3800 cm\(^{-1}\), using a newly developed sub-70 fs broadband infrared source. By probing the entire mid-infrared continuum absorption of aqueous hydroxide solutions with ultrafast pulses, the broadband infrared source allows us to monitor time-dependent changes in this broad spectral window. These experiments, in conjunction with harmonic vibrational analysis of OH\((\text{H}_2\text{O})_{17}\) clusters, reveal that O—H stretch vibrations of aqueous hydroxides arise from coupled vibrations of multiple water molecules solvating the ion. These delocalized vibrations cannot be distinguished based on the local structure of the hydroxide ion. However, they can be classified according to the symmetry defined by the relative phase of vibrations of the O—H bonds hydrogen bonded to the ion. In general, we find the asymmetric O—H stretch vibrations to be more intense and shifted to lower frequencies compared to the symmetric
ones. Analysis of transient absorption and waiting time dependent 2DIR spectroscopy shows that the vibrations in aqueous hydroxide solutions relax on 100-300 fs timescale. Alongside, the O—H stretch vibrations originating from the bulk-like water molecules as well as the asymmetric O—H stretch vibrations of the water molecules solvating the hydroxide ion lose their frequency memory within 160-180 fs. Such loss in frequency memory on similar timescales is likely to happen through migration of vibrational excitation between two types of O—H stretch vibrations.

Spectral features in strongly hydrogen bonded systems like water and aqueous hydroxide solutions are very broad, particularly the induced absorption features in the transient absorption and 2DIR spectra. With the development of broadband mid-infrared pulses, we are able to detect nonlinear response of these systems in the frequency window of 1350-3800 cm\(^{-1}\), observing >1700 cm\(^{-1}\) broad induced absorption features. Qualitatively, strong coupling between intra- and intermolecular vibrations lead to such broadening. In order to explain the experimental results, we have developed a self-consistent phenomenological model that consists of an intramolecular and an intermolecular vibration, with strong nonlinear coupling between them. We find that the experimental results are reproduced when the coupling between the vibrations is strong enough to yield eigenstates with mixed intra- and intermolecular vibrational character. In such scenarios, the identities of individual intra- and intermolecular vibrational modes are lost.

Thesis Supervisor: Andrei Tokmakoff
Title: Professor of Chemistry
To my parents, Anuva and Nikhil Kumar Mandal

And

My wife, Shraboni

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Chapter 1

Introduction

1.1. Water Mediated Proton Transport in Aqueous Solutions:

Water is the most abundant liquid in nature. It plays a pivotal role in various types of chemical and biological reactions, not only by acting as a medium but also by actively dictating the courses of the processes. Charge transport and redox processes occurring in biological systems, fuel cells and various other systems are often directly mediated by water [1–7]. Much of water’s versatile properties are resulted due to the presence of a strong and dynamic hydrogen bonding network. The mobility of protons and hydroxide ions in aqueous solutions of acids and bases are much higher compared to ions of similar size and charge density [8], largely due to the aid of hydrogen bonding network of water. From the mobility data, the estimated barrier for proton transport (PT) is ~2-3 kcal/mol compared to ~5-6 kcal/mol strength of hydrogen bonds in liquid water [9]. Therefore, molecular description of PT in aqueous medium is critically dependent on understanding the role of water’s hydrogen bonding network in the process.

A textbook picture suggests that a proton can be accepted or donated utilizing the hydrogen bonds to the neighboring water molecules, leading to movement of the charge
without long range displacement of a specific set of atoms, thereby resulting anomalously high mobility of protons and hydroxide ions in water [8]. This picture is known as the “Grotthuss mechanism”. In the early nineteenth century, while working on electrolysis in galvanic cells, von Grotthuss suggested that fast charge migration takes place in water due to the presence of “conducting wires” [10]. Concept of chemical bonds were alien at that point of time. The textbook picture of PT draws heavily from Grotthuss’ idea, and hence named after him.

However, such a description of PT in aqueous medium portrays the process to take place along one-dimensional “wires” formed by water’s hydrogen bonds. Moreover, the hydrogen bonding network of liquid water fluctuates on femtoseconds to picoseconds timescale due to various motions of the water molecules [11–14]. The nuclear motions in water such as O—H stretch or H-O-H bend vibrations take place on 10-20 fs timescale, whereas, librations (hindered rotation) and intermolecular hydrogen bond stretches occur on 50 fs and ~150 fs timescale respectively [15–17]. Slower motions like distortion of hydrogen bonds about oxygen centers occur on ~550 fs timescale, whereas, the rearrangement of the liquid takes place on 1-2 ps timescale [18]. Therefore, a complete description of PT in aqueous solutions needs to include the influence of full three-dimensional hydrogen bonding network of water alongside the impact of fast fluctuation in this network. Much of the current understanding of the process is derived from various molecular dynamics (MD) simulations performed over the last few decades, largely due to lack of experimental techniques to probe water’s behavior on fast enough timescales.

The process of PT in aqueous acid and hydroxide solutions have often been described in terms of interconversion between different stable solvated structures of an
excess proton or hydroxide ion. However, there is little consensus regarding the stable solvated structures of either of the species. In the case of excess protons, broadly two different stable structures are proposed: an Eigen cation (H₉O₄⁺) [19], where a hydronium ion (H₃O⁺) is triply solvated and a Zundel cation (H₅O₂⁺) [20], where a proton is equally shared between two water molecules (Fig. 1-1). The role of the first solvation shell water molecules in the PT process has been highlighted by all the proposed mechanisms based on either stable structure [21,22]. Empirical valence-bond MD (EVB-MD) simulations go on to suggest the influence of water molecules in the second solvation shell of the ion in PT [23]. The second solvation shell water molecules rearrange themselves in order to solvate the product of the PT. Amid the controversy regarding the relative stability of the Eigen and Zundel cations, Car-Parrinello MD (CPMD) simulation has identified them as limiting structures of hydrated protons with a possibility of having several short lived structures in between the two [24]. Such results indicate toward a picture of PT that requires consideration of some collective effects in the system rather than changes in the local structure only.

![Illustrations of Eigen (H₉O₄⁺) and Zundel (H₅O₂⁺) cations.](image)

*Figure 1-1:* Illustrations of Eigen (H₉O₄⁺) and Zundel (H₅O₂⁺) cations.
Similar to transport of excess protons in aqueous acids, PT in aqueous hydroxide solutions is often described in terms of stable solvated structures of the hydroxide ion. One such picture proposes the solvated OH\(^-\) complex to be a 3-coordinate H\(_7\)O\(_4\)\(^-\) species in its most stable form, where the OH\(^-\) ion accepts three hydrogen bonds from water and donates none, analogous to the Eigen cation of the excess proton (Fig. 1-2) [25–28]. During PT, a proton becomes equally shared between two OH moieties giving rise to an intermediate Zundel-like H\(_3\)O\(_2\)\(^-\) species (Fig. 1-2). This mechanism is put into question by CPMD and EVB-MD simulations, which observes a 4-coordinate stable structure of solvated OH\(^-\), wherein the OH\(^-\) ion accepts four hydrogen bonds from the surrounding water molecules and donates none (Fig. 1-2) [29–38]. According to this picture, the fluctuations in water structure cause the solvated OH\(^-\) ion to lose one accepting hydrogen bond and to transiently donate one in order to act as a favorable configuration for transfer of a proton from the solvation waters to the ion, a concept known as “pre-solvation”. On the other hand some of the most recent EVB-MD studies suggest even higher coordination number for the OH\(^-\) ion in its most stable form in aqueous solutions [39–41].

![Figure 1-2: Illustrations of 3-coordinate, 4-coordinate and Zundel-like \(H_3O_2^-\) solvated hydroxide complexes.](image)
Most of the structural changes described in any of the PT mechanisms in aqueous hydroxide solutions take place on femtoseconds to picoseconds timescales, similar to fluctuations in water’s hydrogen bonding network. Due to lack of the required time resolution, not a great deal of experimental evidences exist in favor of the mechanisms described above. However, there are evidences in favor both the 3- and 4-coordinate solvated hydroxide complexes from time-averaged experiments. The 3-coordinate stable structure of solvated OH\(^-\) ion is supported by gas-phase infrared (IR) spectroscopy of OH\(^-\)(H\(_2\)O\(_n\)) \((n=1−5)\) clusters [42,43]. On the other hand, neutron scattering [44−47], x-ray diffraction [48] and absorption measurements [49], and core-level photoelectron emission experiments [50] on aqueous NaOH indicate that the average coordination number of the OH\(^-\) ion is 3.9±0.3 at concentrations less than 10M. It also suggest that the OH\(^-\) ion donates a hydrogen bond only transiently, if at all, consistent with the CPMD and EVB-MD simulation results.

The mechanisms for PT in aqueous hydroxide solutions discussed so far, take into account changes in local structure of the OH\(^-\) ions but understates the collective effect of hydrogen bond fluctuation occurring beyond the first solvation shell of the ion. Given that fluctuations in the hydrogen bonding network of water takes place on femtoseconds to picoseconds timescales, it is also likely that the notion of stable solvated structure of the OH\(^-\) ion is instantaneous in nature. Some of the most recent CPMD simulations point towards a multiscale and multidynamical picture of PT, where changes in the hydrogen bonding network of solvating water molecules is proposed to be the guiding factor [51,52]. A proton is proposed to have long range transport across 2-3 water molecules due to contraction of hydrogen bonding network of water, after attaining a favorable
configuration. Attainment of such configurations are proposed to be the key step in the PT process which is uncorrelated to the local structure of the solvated OH⁻ ion. Analysis of EVB-MD simulations also indicate collective electric fields of solvating water molecules along the proton transfer direction to be a the reaction coordinate in such scenarios, rather than changes in local structure of the solvated hydroxide ion [23,53–55].

PT in aqueous hydroxide solution involves dynamical processes on several different timescales. CPMD simulations suggest shuttling motion of a proton in a Zundel-like H₃O₂⁻ species to take place on ~180 fs timescale before localizing with one of the OH moieties in the transition state [34,35,38]. However, a successful transfer of proton takes place on a few picoseconds timescale. Ultrafast nonlinear IR spectroscopy on isotope diluted aqueous hydroxide solutions provide evidences in favor of fleeting existence (~100-120 fs) of the Zundel-like species of during PT [56–58]. On the other hand, it associates a timescale of ~3 ps with successful transfer of protons [57]. Some of the recent CPMD and EVB-MD simulations also suggest that despite having proton shuttling motion on few hundreds of fs timescale, collective rearrangement of the hydrogen bonding network of water favoring successful PT and subsequent solvation of the newly formed OH⁻ ion takes few picoseconds to occur [52,53].

Even though there is limited experimental evidences for the proposed mechanisms of PT in aqueous hydroxide solution, some of the promising results emerge from ultrafast nonlinear IR spectroscopy [56–60]. One aspect that makes it a well-suited tool to study this problem is its time resolution of ~50-100 fs. At the same time, the IR spectral signatures are sensitive to changes in hydrogen bond strength [13,61–63]. In aqueous hydroxides, stronger hydrogen bonding of water molecules with the OH⁻ ion compared to that in the
bulk, results in dramatic redshifts of the O—H stretch vibrational frequencies of the system. It is manifested as a continuum absorption in the linear IR spectra, composed of massively broadened and overlapping peaks that span the mid-IR spectral region (Fig. 1-3) [64–67]. On the other hand, the O—H stretch vibrations in neat liquid water are shown to be delocalized over up to 10 water molecules and strongly coupled to bend and intermolecular vibrations [68–73]. However, the influences of OH⁻ ions on these vibrations are uncertain. There is evidence from ultrafast vibrational and orientational relaxation and charge transfer studies in aqueous hydroxide solutions that point towards a collective nature of the vibrations of solvated OH⁻ complexes [59,60,74]. Use of ultrafast nonlinear IR spectroscopy can report on interaction between different vibrations contained in the broad continuum absorption and changes in them with few tens of fs time resolution. Such information is crucial to describe the molecular origin of the broad absorption feature, which holds the key in explaining the structure and dynamics of the solvated OH⁻ ion.

Figure 1-3: Linear IR spectra of H₂O and 7M NaOH/H₂O. The spectra are normalized to the peak of O—H stretch vibration near 3400 cm⁻¹.
We have developed a <70 fs broadband IR source that spans from <400 cm\(^{-1}\) to 4000 cm\(^{-1}\) [75], in order to probe the continuum absorption feature in aqueous hydroxide solutions. Using ultrafast IR spectroscopy, we excite different types of O—H stretch vibrations and probe the entire mid-IR region with the broadband IR pulse. Cross peak and induced absorption features in these experiments in conjunction with harmonic vibration analysis of solvated OH\(^-\) clusters, provide us information about the vibrational characteristics of solvated hydroxide ions, otherwise unattainable from linear spectra. The vibrations of solvated hydroxide ions turn out to be delocalized and independent of local structure of the ion, but distinguishable in terms of symmetry. Study of their dynamics show that the O—H stretch vibrations arising from bulk-like water molecules and solvated hydroxide ions lose their memory within 160-180 fs after excitation, likely due to migration of vibrational excitation between two types of O—H stretch vibrations.

1.2. IR Spectroscopy of Strongly Hydrogen Bonded Systems:

Our studies on neat water and aqueous hydroxide solutions using ultrafast nonlinear IR spectroscopy investigates the structure and dynamics of water solvated OH\(^-\) ions and vibrational dynamics of these systems. One of the many connecting threads among these systems is presence of strong hydrogen bonding. Linear IR spectra of such strongly hydrogen bonded systems have distinctive shifts and broadening of the spectral features. With the ability to probe the mid-IR spectra in 1350-3800 cm\(^{-1}\) region with the broadband IR pulses, we observe some similarities in the transient absorption (TA) and broadband 2DIR (BB 2DIR) spectral lineshapes of these systems. A combination of ground state bleach and stimulated emission signal corresponding to the fundamental vibrational
frequencies are accompanied by induced excited state absorption features in these spectra. For many aqueous systems including neat water and aqueous hydroxide solutions, the induced absorption feature of O—H stretch vibration resulted on pumping the same is extremely broad (~2000 cm⁻¹) with a long tail that is extended to frequencies lower than our detection limit. Alongside, the vibrational features in these systems relax on few hundreds of fs timescale [72,76,77]. One of the signatures of aqueous systems is appearance of “thermal difference” like spectral features in TA and BB 2DIR experiments after completion of vibrational relaxation, due to structural rearrangement of the liquid on 1-2 ps timescale. However, in neat water and isotopically pure aqueous hydroxide solutions, such features show up almost at the point of excitation, which cannot be resulted due to structural rearrangement of the liquid. This observation alongside unusual width of the induced absorption feature point towards presence of strong coupling between intramolecular (e.g. O—H stretch) and intermolecular (e.g. hydrogen bond stretch) vibrations in these strongly hydrogen bonded systems.

Spectral shifts and broadening in hydrogen bonded systems due to strong coupling between intra- and intermolecular vibrations have been studied for a long time [63,78–94]. Historically, much of these studies emerged in order to explain the experimentally observed linear IR spectral features in strongly hydrogen bonded crystalline substances like alcohols, carboxylic acid dimers, ice, some salts containing hydrogens etc. [78–82,84–86]. Most of these models were two-dimensional, containing two coupled oscillators, one corresponding to an intramolecular vibration and the other corresponding to an intermolecular vibration. The models varied in terms of the form of the individual potentials and the coupling. Most of these models also considered adiabatic separation of the two coordinates while
calculating the energy levels for the system. Such an approximation implies parametric
dependence of the intramolecular vibration on the intermolecular coordinate and the
resulting eigenstates of the system can be represented as two different quantum numbers
for these two modes. In general, the goal of these models were to show that the
anharmonicity of the high frequency intramolecular vibration changes dramatically on
being coupled to a low frequency intermolecular vibration, leading to an array of transitions
with broader ranges of frequencies.

Later on, similar models have been used to examine ultrafast IR spectroscopic
signatures of carboxylic acid dimers and ice. Both these systems happen to have broad
spectral features, particularly broader induced absorption in ice, alongside having very fast
vibrational relaxation. For carboxylic acid dimers, the model considers linear coupling
between the intra- and intermolecular vibrations where the intermolecular vibration is
considered to be harmonic [90–93]. On the other hand, a nonlinear coupling between two
anharmonic oscillators have been considered in case of ice [95–97]. Even though the
models are simplistic in nature for usage in a condensed phase system, they offer significant
insight into the observed broadening of induced absorption feature and vibrational
dynamics. It is argued that strong nonlinear coupling between the vibrational modes along
with non-adiabatic nature of the system contributes to the observed results.

The observed linewidth of spectral features in aqueous solutions are even broader
than ice. At the same time vibrational relaxation timescales are faster or on the same
timescales. We implement a two-dimensional model similar to the one used in case of ice,
in order to get qualitative idea about the origin of the spectral features. We find that strong
nonlinear coupling between intra- and intermolecular vibrations is essential to reproduce
the experimental spectral features, especially the induced absorptions in TA and BB 2DIR spectra. The coupling results strongly mixed intra- and intermolecular characters in the eigenstates of the system, resulting an array of transitions. In such scenarios, where identity of the individual modes are lost, adiabatic separation of intra- and intermolecular vibrations turns out to be a poor approximation.

1.3. Thesis Outline:

In this thesis, I shall describe assignments of IR spectral features and study of vibrational dynamics in aqueous hydroxide solutions using ultrafast nonlinear IR spectroscopy. The spectroscopic observations are complemented by a self-consistent model that describes some of the spectral features observed in TA and BB 2DIR spectra of all aqueous systems.

I shall begin with a brief introduction to third-order nonlinear response functions in chapter 2. The method for calculation of the response functions are discussed in the context of time-dependent perturbation theory. Calculation of response function often requires some approximations. I shall introduce the approximations required to calculate the response functions for simple systems, which will be subsequently used for model systems in this chapter and later in chapter 6.

Chapter 3 will follow up with the details of experimental techniques to acquire TA and BB 2DIR spectra. This chapter will start with providing a description of the ultrafast IR pulse generation and characterization using two different sources. It will also contain information on other important components for the experiment like calibration of translation stages and generation of pulse pairs using an interferometer. Finally a brief
summary of data processing will be presented.

We shall use the experimental techniques described in chapter 3 to perform TA and BB 2DIR spectroscopy on neat water and aqueous NaOH solutions, presented in chapters 4 and 5. Chapter 4 will be devoted to assign features in the linear IR spectra of aqueous hydroxide solution. These assignments are done using results of TA and BB 2DIR spectra in conjunction with harmonic vibration analysis of solvated hydroxide clusters taken from molecular dynamics simulations as snapshots. These assignments pave the way to describe the vibrational dynamics of solvated hydroxide complexes in chapter 5. We shall use waiting time dependent BB 2DIR spectra and TA spectra of aqueous NaOH solutions for studying vibrational dynamics.

Ultrafast nonlinear IR spectroscopy of strongly hydrogen bonded aqueous systems present us some common spectral features that require strong coupling between intra- and intermolecular vibrational modes to explain. We develop a self-consistent model in chapter 6 to understand some of the spectral features observed in chapters 4 and 5.

References:


124517 (2011).


Chapter 2

An Introduction to the Calculation of Third-Order Nonlinear Response Functions

2.1. Introduction:

Infrared (IR) spectroscopy is a widely used technique to study molecular vibrations in condensed phases [1–6]. The environment of molecular vibrations in these systems is under constant fluctuation. Due to its inherent time-averaged nature, linear IR spectroscopy can neither uniquely report on relaxation and dynamics of the vibrational features of a system nor can it inform about interaction between different vibrations. Nonlinear IR spectroscopy is a powerful tool that can track time dependent changes in the vibrational features, interaction between different vibrations, vibrational energy flow and exchange between different molecular species by usage of ultrafast IR pulses [7–15]. The work shown in this thesis uses third-order nonlinear IR spectroscopies to extract such information.

A third-order nonlinear spectroscopy is performed by interacting the system with three time-ordered IR pulses, which generate a signal that is a measure of the third-order
polarization of the sample. Broadly, we have used two different variants of these spectroscopies in this thesis: transient absorption (TA) and 2DIR spectroscopy. In TA, the system has two interactions with the optical pulses, known as pumps, to generate a population state. After a waiting time $\tau_2$, another pulse, known as probe, interacts with the sample and we measure the change in absorption of the probe pulse due to the presence of pump pulses. TA spectroscopy monitors the changes in vibrational population of an excited state as a function of time, and therefore, is very useful to report on vibrational relaxation processes. On the other hand, 2DIR spectroscopy can resolve the third-order nonlinear signal as a function of excitation frequency as well. We use a pair of time-ordered pump pulses to excite the sample in this case. Fourier transform of the time delay between the pump pulses ($T_i$) generates the excitation frequency axis. The waiting time $\tau_2$ is measured by the time delay between the trailing pump pulse and probe pulse. In frequency domain, a 2DIR spectra can be interpreted as probability of exciting a vibration at a given frequency $\omega_1$ and detecting it at another frequency, $\omega_3$, after a waiting time $\tau_2$. Coupling between different vibrations can be detected through cross peaks in 2DIR spectra. A series of 2DIR spectra collected as a function of $\tau_2$ also inform about spectral diffusion, which is a measure of how the correlation between excited and detected vibrational frequencies is lost. These $\tau_2$ dependent spectra are useful in understanding vibrational energy transfer and exchange between two chemical species with different vibrational signatures through the changes in the cross peak features [11,14].

In this chapter, I shall provide a brief introduction to the formalism of third-order nonlinear spectroscopy within the context of time-dependent perturbation theory. The signal is related to the third-order polarization of the system, which is obtained from the
third-order nonlinear response functions. Equations for calculation of the third-order response functions require some input parameters, some of which can be obtained from experimental observables. Often it is tough to get all the parameters from experiments and molecular dynamics (MD) simulations can be of help in such situations. At the same time, calculation of the response functions require some approximations, some of which are discussed in this chapter. Finally, we shall use the developed methodology to calculate 2DIR spectra for a model four-level system, which will be extensively used in Chapter 6 for strongly coupled vibrational systems.

2.2. Formulation of Third-order Nonlinear Response Functions:

In third-order nonlinear spectroscopy experiments, the system interacts with three time ordered pulses and the signal is emitted due to the third-order polarization created in the sample. We start describing the process by defining the total time-dependent Hamiltonian for the sample interacting with the optical pulses:

\[ H_{\text{total}}(t) = H_{\text{sample}} + H_{\text{light}} + H_{\text{int}}(t) \]  

(2-1)

Here, \( H_{\text{total}} \) describes the total Hamiltonian of the process that consists of the Hamiltonian for the sample \( (H_{\text{sample}}) \), the optical pulses \( (H_{\text{light}}) \) and the time-dependent light-matter interaction \( (H_{\text{int}}) \). In this formalism, we are interested in studying the effect of the incident optical pulses on the sample, and therefore, we do not explicitly consider changes in the pulses due to interaction with the sample. Thus, the Hamiltonian for the pulses, \( H_{\text{light}} \) is neglected in the subsequent discussion.

The sample Hamiltonian \( (H_{\text{sample}}) \) is further subdivided three parts: a part that is
resonant with the input pulses, called system \( H_{\text{system}} \), the other part that acts as a bath \( H_{\text{bath}} \) along with a system-bath interaction component \( H_{\text{sys-bath}} \). The system consists of vibrational modes that interacts with the incident optical pulses, whereas, the bath modes do not directly interact with the pulses. Instead, the bath interacts with the system to indirectly impact the eigenstates of the system.

\[
H_{\text{sample}} = H_{\text{system}}(p, q) + H_{\text{bath}}(P, Q) + H_{\text{sys-bath}}(p, q, P, Q)
\]  

(2-2)

Here, the lowercase and uppercase variables are used for the system and the bath, respectively.

We perform the third-order nonlinear spectroscopies on aqueous solutions. In these samples, the light-matter interaction occurs on molecular length scale, typically few angstroms, which is much smaller than the wavelength of the optical pulses. Therefore, we can use dipole approximation for calculating the light-matter interaction, \( H_{\text{int}} \), which treats the dipole moment of the sample to be driven by the electric field of the incident optical pulses.

\[
H_{\text{int}}(t) = -\mu(q, Q, t) \cdot E(r, t)
\]  

(2-3)

Here, \( \mu(q, Q, t) \) is the dipole moment operator of the sample. For many vibrational systems, the dipole moment operator depends only on the system coordinate, \( q \) (Condon approximation, discussed in detail in section 2.4). However, in some scenarios like strongly hydrogen bonded systems, non-Condon and electrical anharmonicity effects are described through a dependence of the dipole moment operator on \( Q \) [16,17]. \( E(r, t) \) is the electric field of the optical pulses as a function of position and time coordinates:
\( \mathbf{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r}) \cdot e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + c.c. \) \hfill (2-4) 

Interaction of optical pulses with the sample generates a time-dependent macroscopic polarization that subsequently emits the signal. The total macroscopic polarization of the sample \( \mathbf{P}(\mathbf{r}, t) \), on interaction with optical pulses can be obtained from:

\[
\mathbf{P}(t) = Tr\left[ \mu(\mathbf{q}, \mathbf{Q}, t) \rho(t) \right] \tag{2-5}
\]

Where, \( \rho(t) \) represents the density matrix of the sample. The time evolution of the density matrix of the sample is governed by Liouville-von Neumann equation:

\[
i\hbar \frac{\partial \rho(t)}{\partial t} = \left[ H_{\text{total}}(t), \rho(t) \right] \tag{2-6}
\]

The total Hamiltonian \( H_{\text{total}} \) for the process includes a time-independent sample part \( H_{\text{sample}} \) and a time-dependent light-matter interaction part \( H_{\text{int}} \). Such problems are often convenient to work in the interaction picture. We substitute the density matrix and the light-matter interaction Hamiltonian by their forms in the interaction picture \( \rho_I(t) \) and \( H_{\text{int}}^I \) respectively) in Eq. 2-5 to transform the Liouville-von Neumann equation, as shown in Eq. 2-7.

\[
\rho_I(t) = e^{\frac{-iH_{\text{sample}}^I}{\hbar}} \rho(t) e^{\frac{iH_{\text{sample}}^I}{\hbar}} \tag{2-7A}
\]

\[
H_{\text{int}}^I(t) = e^{\frac{-iH_{\text{sample}}^I}{\hbar}} H_{\text{int}}(t) e^{\frac{iH_{\text{sample}}^I}{\hbar}} \tag{2-7B}
\]

\[
i\hbar \frac{\partial \rho_I(t)}{\partial t} = \left[ H_{\text{int}}^I(t), \rho_I(t) \right] \tag{2-7C}
\]
The Liouville-von Neumann equation can be solved by integrating both sides of eq. 2-7C with respect to time and iteratively substituting the result onto itself. Such a solution results the density matrix in the interaction picture as a sum of time ordered integrals, as shown in Eq. 2-8.

\[ \rho_1(t) = \sum_{n=0}^{\infty} \rho_1^{(n)}(t) \]  

(2-8A)

\[ \rho_i^{(n)}(t) = \left( -\frac{i}{\hbar} \right)^n \int_{-\infty}^{t} dt_n \int_{-\infty}^{t_{n-1}} dt_{n-1} \cdots \int_{-\infty}^{t_1} dt_1 \left[ H_{in}^{I}(t_n), \left[ H_{in}^{I}(t_{n-1}), \ldots, \left[ H_{in}^{I}(t_1), \rho_i^{(0)} \right] \right] \right] \]  

(2-8B)

In this expression, \( t_m \) represents the time-interval between the interactions of the \( m \)th and the \( m+1 \)th pulse and \( n \) denotes the order of nonlinearity determined by the number of light-matter interactions resulting that term. \( \rho_i^{(0)} \) represents the equilibrium density matrix, \( \rho_{eq} \).

In order to obtain a solution for the macroscopic polarization, we use results of Eq. 2-7A and Eq. 2-8 in the expression for density matrix in Eq. 2-5. We end up with a similar perturbative expression for the polarization, where each term corresponds to a different number of light-matter interactions.

\[ \mathbf{P}(t) = \sum_{n=1}^{\infty} \mathbf{P}^{(n)}(t) \]  

(2-9)

The first term corresponds to interaction of the sample with one optical pulse and thereby contains information about the linear absorption and emission properties of the sample. Due to symmetry constrains, all the even order polarization terms vanish in an isotropic sample like the one used by us [18]. Therefore, the lowest order nonlinear polarization we
can detect is the third-order one, as given by Eq. 2-10.

\[
P^{(3)}(t) = \int_0^\infty \int_0^\infty \int_0^\infty dt_1 dt_2 dt_3 R^{(3)}(t_1, t_2, t_3) E_\alpha(t-t_3) E_\beta(t-t_3-t_2) E_\gamma(t-t_3-t_2-t_1)
\]  

(2-10)

Here, \( R^{(3)}(t_1, t_2, t_3) \) denotes the third-order nonlinear response function and \( E_\alpha \) are the electric field envelope of the interacting pulses. Time delay between the pulses \( E_\alpha \) and \( E_\beta \) is \( t_1 \) and the same between \( E_\beta \) and \( E_\gamma \) is \( t_2 \). On the other hand, the signal is detected a time \( t_3 \) after the interaction of the third pulse \( E_\gamma \). Equation 2-10 accounts for the finite duration of the interacting optical pulses by including the field envelopes in the expression of the third-order nonlinear polarization. However, for delta function pulses, the integrals in Eq. 2-10 disappear, and the third-order nonlinear polarization becomes proportional to the third-order nonlinear response function. The third-order nonlinear response function can be expressed in terms of nested commutators of dipole moment operators of the sample:

\[
R^{(3)}(t_1, t_2, t_3) = \left( \frac{i}{\hbar} \right)^3 \Theta(t_1) \Theta(t_2) \Theta(t_3) \left\{ \left[ \left[ \mu(t_3 + t_2 + t_1), \mu(t_2 + t_1) \right], \mu(t_1) \right], \mu(0) \right\}
\]  

(2-11)

The Heaviside step functions, \( \Theta(t) \) are introduced to enforce causality and angular bracket denotes an ensemble average over the sample degrees of freedom. The dipole moment operators in Eq. 2-11 are in the interaction picture, \( \mu(t) = e^{iH_{\text{sample}} t/\hbar} \mu(q, Q)e^{-iH_{\text{sample}} t/\hbar} \).

The resulted macroscopic polarization due to interaction of the sample with optical pulses can be thought as a source of electromagnetic radiation, equivalent to an accelerating
charge. The signal electric field ($E_{\text{sig}}$) is related to the macroscopic polarization through Maxwell’s equation and can be related to the time derivative of the polarization (Eq. 2-12). The macroscopic polarization contains an oscillatory term with the frequency of the signal, therefore, the signal field is $\pi/2$ phase shifted from the polarization.

$$E_{\text{sig}}(t) \propto \frac{\partial P^{(3)}(t)}{\partial t}$$  \hspace{1cm} (2-12)

The direction in which the signal electric field is emitted and its frequency depends on the electric field wavevectors and frequencies of the incident optical pulses as shown in 2-13.

$$k_{\text{sig}} = \pm k_x \pm k_y \pm k_z$$  \hspace{1cm} (2-13A)

$$\omega_{\text{sig}} = \pm \omega_x \pm \omega_y \pm \omega_z$$  \hspace{1cm} (2-13B)

2.3. Approximations in Calculation of Third-Order Nonlinear Response Functions:

The expression for the third-order nonlinear response function given in Eq. 2-11 contains nested commutators of dipole moment operators. Expansion of the expression leads to eight terms containing products of dipole moment operators, of which only 4 are unique and the rest are complex conjugates of them.

$$R^{(3)}(t_3, t_2, t_1) = \left( \frac{i}{\hbar} \right)^3 \Theta(t_1) \Theta(t_2) \Theta(t_3) \sum_{i=1}^{4} [R_i(t_1, t_2, t_3) - R_i^*(t_1, t_2, t_3)]$$  \hspace{1cm} (2-14)

The individual terms $R_i(t_1, t_2, t_3)$ can be written as sum over all possible intermediate states in the eigenstate representation, as shown in Eq. 2-15.
\[
\begin{align*}
R_1(t_3, t_2, t_1) &= \sum_{abcd} P_a \langle \mu_{ab}(t_3 + t_2 + t_1) \mu_{bc}(t_2 + t_1) \mu_{cd}(t_1) \mu_{da}(0) \rangle \\
R_2(t_3, t_2, t_1) &= \sum_{abcd} P_a \langle \mu_{ab}(t_1) \mu_{bc}(t_2 + t_1) \mu_{cd}(t_3 + t_2 + t_1) \mu_{da}(0) \rangle \\
R_3(t_3, t_2, t_1) &= \sum_{abcd} P_a \langle \mu_{de}(t_1) \mu_{eb}(t_3 + t_2 + t_1) \mu_{ba}(t_2 + t_1) \mu_{ad}(0) \rangle \\
R_4(t_3, t_2, t_1) &= \sum_{abcd} P_a \langle \mu_{de}(t_2 + t_1) \mu_{eb}(t_3 + t_2 + t_1) \mu_{ba}(t_1) \mu_{ad}(0) \rangle \\
\end{align*}
\]

(2-15)

Here, the set of indices \((a, b, c, d)\) represents the eigenstates of the system. The transition dipole matrix elements in each of these terms are given by \(\mu_{ij}(t) = \langle i | \mu(t) | j \rangle\).

As the system is at equilibrium, the density matrix is diagonal at time 0. Therefore, \(P_a\) denotes the probability of having the system in eigenstate \(a\) at time 0, which is given by

\[
P_a = \frac{e^{-E_a/k_BT}}{\sum_a e^{-E_a/k_BT}}.
\]

Equation 2-15 can be re-written by explicitly writing down the time evolution operators of the transition dipole matrix elements as:

\[
\begin{align*}
R_1(t_3, t_2, t_1) &= \sum_{abcd} P_a \langle e^{iH_a(t_3+t_2+t_1)/\hbar} \mu_{ab} e^{-iH_b(t_1)/\hbar} \mu_{bc} e^{-iH_c(t_2)/\hbar} \mu_{cd} e^{-iH_d(t_1)/\hbar} \mu_{da} \rangle \\
R_2(t_3, t_2, t_1) &= \sum_{abcd} P_a \langle e^{iH_d(t_1)/\hbar} \mu_{ab} e^{iH_b(t_2)/\hbar} \mu_{bc} e^{iH_c(t_1)/\hbar} \mu_{cd} e^{iH_d(t_2)/\hbar} \mu_{da} \rangle \\
R_3(t_3, t_2, t_1) &= \sum_{abcd} P_a \langle e^{iH_d(t_3+t_1)/\hbar} \mu_{de} e^{iH_e(t_1+t_2)/\hbar} \mu_{eb} e^{iH_b(t_2)/\hbar} \mu_{ba} e^{iH_a(t_1+t_2)/\hbar} \mu_{ad} \rangle \\
R_4(t_3, t_2, t_1) &= \sum_{abcd} P_a \langle e^{iH_d(t_3+t_1)/\hbar} \mu_{de} e^{iH_e(t_1+t_2)/\hbar} \mu_{eb} e^{iH_b(t_2)/\hbar} \mu_{ba} e^{iH_a(t_1+t_2)/\hbar} \mu_{ad} \rangle \\
\end{align*}
\]

(2-16)

Where, \(H_\alpha = \langle \alpha | H_{\text{sample}} | \alpha \rangle\) for \(\alpha = a, b, c, d\).

Evaluation of the third-order nonlinear response function through Eq. 2-16 requires to sum over all the eigenstates and all possible excitation pathways. However, for most condensed phase systems, the number of pathways can escalate to a very large number with increase in the number of available eigenstates. However, many of these terms involve
transitions between states of the system that are not resonant with the excitation pulses used in the experiment and can be ignored. This assumption is known as the rotating wave approximation [7] and holds well for most vibrational systems. Experimental constraints allow us to further neglect some of other terms. The TA and 2DIR experiments shown in this thesis are performed in the pump-probe geometry, as discussed in chapter 3. The signal co-propagating with the probe pulse is detected in this geometry. These experimental conditions only detect rephasing and non-rephasing signals, with wavevector matching conditions $k_{sig} = -k_x + k_y + k_y$ and $k_{sig} = k_x - k_y + k_y$, respectively. Even after imposing these constraints, it is useful to make some approximations to simplify the calculation of third-order nonlinear response functions [13,14,19,20].

One of the approximations we make use of is the Condon approximation, which states that the dipole moment for the sample only depends on the system coordinates and it has no dependence on the bath coordinates. The angular brackets in Eq. 2-16 denotes ensemble averaging over the bath degrees of freedom. Therefore, within Condon approximation, we can take the transition dipole matrix elements in Eq. 2-16 out of the angular bracket and re-write the expression for the third-order nonlinear response functions as below:

\[
\begin{align*}
R_1(t_3, t_2, t_1) &= \sum_{abcd} P_{ab} \mu_{bc} \mu_{cd} \mu_{da} \left< e^{iH(t_3+t_2+t_1)/\hbar} e^{-iH(t_1)/\hbar} e^{-iH(t_2)/\hbar} e^{iH(t_3)/\hbar} \right> \\
R_2(t_3, t_2, t_1) &= \sum_{abcd} P_{ab} \mu_{bc} \mu_{cd} \mu_{da} \left< e^{iH(t_3)/\hbar} e^{iH(t_2)/\hbar} e^{-iH(t_1)/\hbar} e^{-iH(t_3)/\hbar} \right> \\
R_3(t_3, t_2, t_1) &= \sum_{abcd} P_{ab} \mu_{bc} \mu_{cd} \mu_{da} \left< e^{iH(t_3)/\hbar} e^{iH(t_2+t_1)/\hbar} e^{-iH(t_3)/\hbar} e^{-iH(t_3)/\hbar} \right> \\
R_4(t_3, t_2, t_1) &= \sum_{abcd} P_{ab} \mu_{bc} \mu_{cd} \mu_{da} \left< e^{iH(t_3+t_1)/\hbar} e^{-iH(t_2)/\hbar} e^{-iH(t_2)/\hbar} e^{-iH(t_3)/\hbar} \right>
\end{align*}
\]

(2-17)

The Condon approximation does not work very well for hydrogen bonded systems.
It has been shown that absorption cross-section for O—H stretch vibrations in water increases at lower frequencies, i.e. when the O—H bond forms stronger hydrogen bonds. These effects are particularly observed in case of isotope diluted studies of water and aqueous hydroxides [17,21–24]. Influence of bath on the O—H stretch transition dipole is likely resulted by influence of intermolecular vibrational modes on the O—H stretch. However, to calculate third-order nonlinear response function for qualitative comparison with the experiments and for inexpensive calculations, we make use of this approximation for aqueous systems in chapter 6.

Within the Condon approximation, the expression for the third-order nonlinear response functions still possess time-ordered exponentials (Eq. 2-17), which are difficult to evaluate without a quantum dynamical trajectory or classical frequency trajectory [25]. In order to convert the time-ordered exponentials to ordinary exponentials, we have used the second cumulant approximation [7]. This approximation introduces energy gap correlation functions (Eq. 2-18) and assumes a Gaussian dynamics for the transition frequencies. Thereby the approximation leads to cancellation of all higher order moments of transition frequencies beyond second order. This approximation works when the bath degrees of freedom are harmonic in nature and the system-bath coupling is weak and linear.

\[ C_j(t) = \langle \delta \omega_{j0}(t) \delta \omega_{j0}(0) \rangle \tag{2-18} \]

Here, \( i \) and \( j \) are two eigenstates of the system whose energy gap correlation is measured with respect to the ground state. \( \omega_{j0} = \frac{(E_i - E_0)}{\hbar} \) and \( \delta \omega_{j0}(t) = \omega_{j0}(t) - \langle \omega_{j0} \rangle \). Within Condon and second cumulant approximations, the third-order nonlinear response functions of Eq. 2-17 can be re-written in terms of dephasing functions (Eq. 2-19 to 2-21)
using the energy gap correlation functions as input parameters [19,26].

\[
R_1(t_3,t_2,t_1) = \sum_{abcd} P_{abcd} e^{-i\omega t_3} e^{-i\omega t_2} e^{-i\omega t_1} F^{(1)}_{abcd}(t_3,t_2,t_1)
\]

\[
R_2(t_3,t_2,t_1) = \sum_{abcd} P_{abcd} e^{-i\omega t_3} e^{-i\omega t_2} e^{-i\omega t_1} F^{(2)}_{abcd}(t_3,t_2,t_1)
\]

\[
R_3(t_3,t_2,t_1) = \sum_{abcd} P_{abcd} e^{-i\omega t_3} e^{+i\omega t_2} e^{+i\omega t_1} F^{(3)}_{abcd}(t_3,t_2,t_1)
\]

\[
R_4(t_3,t_2,t_1) = \sum_{abcd} P_{abcd} e^{-i\omega t_3} e^{+i\omega t_2} e^{+i\omega t_1} F^{(4)}_{abcd}(t_3,t_2,t_1)
\]

(2-19)

Here, the dephasing functions \(F^{(a)}_{abcd}(t_3,t_2,t_1)\) can be expressed in terms of the energy gap correlation function as follows:

\[
- \ln \left[ F^{(1)}_{abcd}(t_3,t_2,t_1) \right] = h_{bb}(t_3) + h_{cc}(t_2) + h_{dd}(t_1) + h_{bc}^+(t_3,t_2)
\]

\[
+ h_{ca}^+(t_3,t_2) + f_{ba}(t_3,t_1)
\]

\[
- \ln \left[ F^{(2)}_{abcd}(t_3,t_2,t_1) \right] = \left[ h_{cc}(t_3) \right] + \left[ h_{bb}(t_2) \right] + h_{dd}(t_1 + t_2 + t_3) + \left[ h_{bc}^+(t_3,t_2) \right]^2
\]

\[
+ h_{ca}^+(t_3,t_2 + t_1 + t_3) + f_{ba}(t_3,t_1 + t_2 + t_3)
\]

\[
- \ln \left[ F^{(3)}_{abcd}(t_3,t_2,t_1) \right] = \left[ h_{bb}(t_3) \right] + h_{cc}(t_1 + t_2) + h_{dd}(t_1) + h_{bc}^+(t_3 + t_2, t_1)
\]

\[
- f_{ba}^+(t_3,t_3 + t_2 + t_2) - f_{ba}^+(t_3,t_1 + t_2)
\]

\[
- \ln \left[ F^{(4)}_{abcd}(t_3,t_2,t_1) \right] = h_{cc}(t_3) + h_{dd}(t_2 + t_1) + \left[ h_{bb}(t_3 + t_2) \right] - h_{bc}^+(t_3,t_3)
\]

\[
+ h_{ca}^+(t_2 + t_1 + t_3) - f_{ba}^+(t_2 + t_1 + t_3 + t_2; t_3)
\]

(2-20)

Where:

\[
h_b(t) = \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 C_0(\tau_2 - \tau_1)
\]

\[
h_c(t_2,t_1) = \int_0^{t_2} d\tau_2 \int_0^{\tau_2} d\tau_1 C_0(\tau_2 - \tau_1)
\]

\[
f_{ba}^+(t_2,t_1) = \int_0^{t_2} d\tau_2 \int_0^{\tau_2} d\tau_1 C_0(\tau_2 - \tau_1)
\]

(2-21)

Using Eq. 2-19 to 2-21 to calculate the third-order nonlinear response functions
only require the energy gap correlation function as the input. The energy gap correlation functions can be guessed from the experimental observables and provides a measure of spectral diffusion of the system vibrations. However, the second cumulant approximation yields erroneous lineshapes when the dynamics is non-Gaussian.

**Figure 2-1:** Double sided Feynman diagrams corresponding to (A) non-rephasing ($k_{\text{sig}} = k_\alpha - k_\beta + k_\gamma$), (B) rephasing ($k_{\text{sig}} = -k_\alpha + k_\beta + k_\gamma$) and (C) double quantum coherence ($k_{\text{sig}} = k_\alpha + k_\beta - k_\gamma$) pathways emerging from the third-order nonlinear response functions given by Eq. 2-17 or 2-19. Roman numerals on top of each diagram corresponds to the Arabic numeral of the corresponding response function in Eq. 2-17 or 2-19. The complex conjugate of the response functions are denoted by (*) mark.

The results of Eq. 2-17 or Eq. 2-19 involves different pathways contributing to the
third-order nonlinear response functions. These pathways can be represented with the help of double sided Feynman diagrams, as shown in Fig. 2-1 [7]. In these diagrams, the solid vertical lines represent ket and bra side of the density matrix. The arrowhead lines intersecting the vertical lines represent interaction of optical pulses. Absorption and emission processes are represented by inward and outward pointing lines, respectively. The ket side interactions occur on the left side of the vertical line, whereas, the bra side interactions occur on the right. The time evolution in these diagrams are upwards and during each time interval, the density matrix evolves under the Hamiltonian for the sample. These Feynman diagrams are very useful to keep track of all possible pathways in a particular system.

2.4. Third-Order Nonlinear Response Functions for a 4-Level System:

We shall apply the methodology developed in the earlier sections to calculate the third-order nonlinear response functions for a simple 4-level system. Often we calculate the third-order nonlinear response functions at finite temperatures. Thus, few of the lowest energy eigenstates of the system have significant equilibrium population. These states constitute a ground state manifold from which fundamental transitions can take place. Dipole allowed transitions can take place from these states to multiple eigenstates of the system, constituting the first excitation manifold. Similarly second and higher excitation manifolds contain multiple eigenstates of the system. For the sake of simplicity, we choose a system which has two eigenstates each in the ground, first and second excited manifolds, as shown in Fig. 2-2. Double sided Feynman diagrams shown in Fig. 2-1 can only use up to 4 different eigenstates out of the available 6 in one single pathway, therefore, we refer it
as a 4-level system. When we consider the rephasing and non-rephasing contributions only, the third-order nonlinear response function is comprised of 96 such pathways, provided transition between all the eigenstates in subsequent excitation manifolds are allowed.

![Diagram](image)

**Figure 2-2:** A schematic diagram showing a model 4-level system. The system has two eigenstates in each of its ground, first and second excited manifold. The blue and cyan arrows represent transition energies corresponding to fundamental and overtone transitions respectively.

We consider the rephasing and non-rephasing contributions to third-order nonlinear response function only, as our experiments in pump-probe geometry can detect them only. We have used Eq. 2-19 to 2-21, in order to calculate the response function and the only input parameter we require for that is the energy gap correlation functions. For simplicity, we consider the energy gap correlation function to the same for all the energy gaps (Table 2-1). The calculated response function in time domain is Fourier transformed in $t_1$ and $t_3$ to obtain a frequency domain representation of the same (Fig. 2-3), when $t_2$ is kept fixed at 0.
This frequency domain representation of the response function is the 2DIR spectrum in the limit of delta function pulses.

**Table 2-1:** Parameters used for the energy gap correlation function used in the calculation shown in Fig. 2-3. \( C_0(t) = ae^{\frac{-t}{T_1}} + be^{\frac{-t}{T_2}} \left[ \cos(\Omega t) + \left( \frac{1}{T_2\Omega} \right) \sin(\Omega t) \right] \) is the form of the correlation function used.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>( 4 \times 10^{-6} ) fs(^{-2} )</td>
</tr>
<tr>
<td>( b )</td>
<td>( 5 \times 10^{-6} ) fs(^{-2} )</td>
</tr>
<tr>
<td>( T_1 )</td>
<td>150 fs</td>
</tr>
<tr>
<td>( T_2 )</td>
<td>120 fs</td>
</tr>
<tr>
<td>( \Omega )</td>
<td>175 cm(^{-1} )</td>
</tr>
</tbody>
</table>

**Figure 2-3:** 2DIR spectra for a model 4-level system, as shown in Fig. 2-2. The calculation used Eq. 2-19 to 2-22 with the parameters provided in table 2-1.
The 2DIR spectra has contributions from different transition frequencies in both the bleach (blue) and induced absorption (red) features. We shall use this method for calculating 2DIR spectra of systems which consist of numerous such 4-level systems in chapter 6.

References:


Chapter 3

Generation of Ultrafast Mid-Infrared Pulses and Measurement of Nonlinear Infrared Signals

3.1. Introduction:

Infrared (IR) spectroscopy measures characteristic frequencies, intensities and lineshapes of molecular vibrations. Hydrogen bonding interactions lead to significant frequency shifts, line broadening, and changes in intensities to the spectral features of molecular vibrations [1–4]. Liquid water possesses strong hydrogen bonding between water molecules. As a result, the O—H stretch vibrations redshift and H-O-H bend vibrations blueshift in liquid water compared to their gas phase spectra. Alongside, the widths of these vibrations are on the order of a few hundreds of wavenumbers in the liquid phase [5–8]. In aqueous hydroxide solutions, hydrogen bonds between OH\(^{-}\) ion and the solvating water molecules are stronger compared to hydrogen bonds in neat liquid water. This effect is manifested as a broad continuum absorption in the mid-IR region (1000–4000 cm\(^{-1}\)), including redshift of O—H stretch and blueshift of H-O-H bend vibrations compared to neat liquid water [9–11]. In a nutshell, molecular vibrations of water molecules are good
reporters of their surrounding hydrogen bonding environments in aqueous medium. Inhomogeneity in the local environment of the water molecules are reflected in the broadening of spectral lineshapes in these systems [12–14].

The hydrogen bonding network in liquid water and aqueous solutions undergo changes on femtoseconds to picoseconds timescale [15,16]. These fluctuations include inertial motions of the water molecules to structural rearrangement of the liquid. Proton transport (PT) process in aqueous hydroxide solutions is aided by the hydrogen bonding network of water and its fluctuations play a crucial role in PT. A complete description of PT necessitates, in part, an understanding of the interactions between different vibrations in aqueous hydroxide solution and how they evolve as a function of time. Therefore, a suitable technique to study PT in aqueous hydroxide solution needs to be fast enough to probe the fluctuations in the hydrogen bonding network, alongside being sensitive to changes in local hydrogen bonding environment. With time resolution of <100 fs, sensitivity to probe the local hydrogen bonding environment of water molecules in aqueous medium and the ability to report on the interactions between different vibrations; ultrafast nonlinear IR spectroscopy is well suited for this purpose.

Optical parametric amplifiers (OPA) most frequently serve as the source for ultrafast IR pulses used in nonlinear IR spectroscopy experiments. Commonly used OPAs based on BBO-AgGaS$_2$ create mid-IR output pulses by a difference frequency generation process involving two near-IR pulses, generated using short 800 nm input pulses. Usually, temporal width of these transform limited mid-IR pulses are ~100 fs, corresponding to a full width at half maximum (FWHM) bandwidth of ~200 cm$^{-1}$ [17,18]. On the other hand, O—H stretch vibration in aqueous solutions has FWHM of ~400 cm$^{-1}$. Therefore, in order
to probe the entire O—H stretch lineshape and study faster dynamics in aqueous medium, pulses with larger bandwidth and shorter temporal width are required. Using sub-25 fs 800 nm pulses as an input into a home-built OPA [19], our group has been able to generate sub-45 fs pulses centered around 3 μm (3000-3500 cm⁻¹), coincident with the absorbance of O—H stretch vibration in aqueous solutions. This OPA uses a down-conversion of amplified 800 nm pulses using a KNbO₃ crystal. Temporal width of the mid-IR pulses in our OPA has been reduced by use of very few transmissive optics, careful control of their thickness in order to minimize the dispersion of the pulses and large phase matching bandwidth of KNbO₃ crystal. As the FWHM bandwidth of the transform limited pulses are ~400 cm⁻¹, it allows us to study the dynamics of the O—H stretch vibrations in aqueous solution. However, the tunability of our OPA is fairly limited (center frequency of 3000-3500 cm⁻¹) and hence it can only generate mid-IR pulses centered around 3 μm region of the spectrum.

In order to study structure and dynamics of solvated OH⁻ ions, the continuum absorption in aqueous hydroxide solutions between 1000-4000 cm⁻¹ needs to be probed. Unfortunately, there is no tunable OPA that can probe the entire region between 1000 and 4000 cm⁻¹ in one shot. We have developed an ultrafast broadband IR (BBIR) source in our group that probes the entire region of the spectra with a time resolution of <70 fs [20]. Generation of BBIR pulses involve no difference frequency generation or down-conversion process. Instead, we focus collinearly propagating fundamental, second and third harmonic of sub-25 fs 800 nm pulses in dry air to generate a plasma that produces the BBIR pulses. With the spectral width of the BBIR pulses, we can have access to a wealth of information on processes marked by transitions across the entire mid-IR region,
especially on vibrational relaxation of water and aqueous hydroxide solutions.

The ultrafast IR pulses thus generated, are used to perform two dimensional infrared spectroscopy (2DIR) and transient absorption spectroscopy (TA). These third order nonlinear spectroscopies report on vibrational coupling and dynamics with a time resolution of <100 fs. Strongly interacting vibrations in neat liquid water and aqueous hydroxide solutions are influenced by the hydrogen bond dynamics of the system on femtoseconds to picoseconds timescale. We aim to understand the nature of these vibrations and their time-dependent changes using 2DIR and TA spectroscopies.

In this chapter, I shall first provide an overview of the experimental setup for 2DIR and TA spectroscopy. Generation of ultrafast IR pulses using OPA and BBIR sources and their characterization will be discussed in the subsequent sections. Finally, I shall describe the detailed procedure for acquisition of 2DIR and TA spectra, shown in Chapters 4 and 6.

3.2. Overview of Experimental Setup:

Figure 3-1 shows an overview of the experimental setup for 2DIR and TA experiments that uses ultrafast mid-IR pulses generated by the OPA and BBIR source. Both the OPA and the BBIR generation process uses sub-25 fs 800 nm pulses from a commercial Ti:sapphire amplifier as input. A Femtolasers Femtosource Scientific Pro Ti:sapphire oscillator (76 MHz repetition rate, ~450 mW mode-locked power, 90-100 nm FWHM bandwidth, 10 fs temporal width of pulses), pumped with 4 W output of a Nd:YVO4 Spectra Physics Millennia Vs laser, produces the seed for amplification in the Coherent Legend Elite USX HE regenerative amplifier. Before it is sent for amplification, the seed pulses pass through a spectral filter (Coherent external SSF) that removes intensity from...
**Figure 3-1:** An overview of the experimental setup for 2DIR and TA spectroscopy. Ultrafast mid-IR pulses are generated using OPA and BBIR sources, pumped by sub-25 fs 800 nm pulses out of a commercial Ti:sapphire amplifier. The pulses out of the OPA go into a Mach-Zehnder interferometer to generate a time ordered pulse pair. A time delay $T_2$ is introduced in the 800 nm input of BBIR source. The 3 μm and BBIR pulses are subsequently used for 2DIR and TA experiments. The arrows in the figure show the beam path.

its spectral center, restricting for the gain narrowing which occurs upon amplification (Fig. 3-2). The shaped seed pulses are temporally stretched using a grating-based stretcher and sent to the Ti:sapphire regenerative amplifier. The Ti:sapphire crystal in the amplifier is cooled thermo-electrically inside an enclosure purged with dry air. The ~21.5 W output from a Coherent Evolution 30 (1 kHz, 30 W maximum power, 532 nm) laser serves as the pump for the amplification. After amplification, a beamsplitter splits the 800 nm beam into two arms. One of the arm contains ~1 mJ/pulse energy and is sent to the OPA through a grating compressor. The rest of the amplifier energy (~4 mJ/pulse) is put in the other arm that feeds the BBIR setup after passing through a different grating compressor. The output power of each of the arms are controlled by $\lambda/2$ waveplates. With two separate
compressors, we can pre-compensate for the dispersion in the OPA and BBIR setup independently. Overall, we get a S-polarized 800 nm output from the amplifier with ~5 W power at 1 kHz repetition rate, <25 fs pulse duration and ~65 nm FWHM bandwidth.

Figure 3-2: (Blue) Spectrum of the pulses out of the oscillator that acts as a seed for amplification. (Green) Oscillator spectrum after it passes through the spectral filter (Coherent external SSF). (Red) Spectrum of the amplifier pulse output. All the spectra are normalized to their maximum intensity for comparison.

A BBO-KNbO$_3$ based home-built OPA is pumped with approximately 600 mW power of the 800 nm pulses from the lower energy output arm of the amplifier. The OPA generates sub-45 fs mid-IR pulses centered around 3 µm (3000-3500 cm$^{-1}$). A 2 mm thick, anti-reflection (AR) coated Ge window is used as the last optic in the OPA which removes the residual visible and near-IR light from 3 µm output and compensates for its dispersion during the generation process. For aid in alignment, the OPA output is spatially overlapped on the same Ge window with a HeNe tracer beam. Subsequently, the OPA output is sent
to a Mach-Zehnder interferometer for generation of collinearly propagating pulse pairs. A Mach-Zehnder interferometer generates two identical pulse pairs propagating perpendicular to each other. One of the pulse pairs is subsequently used in 2DIR and TA spectroscopy performed in the pump-probe geometry. The other one is sent to a room temperature HgCdTe (MCT) detector (Electro-Optical Systems Inc.) for obtaining field autocorrelation of the 3 μm pulses. The field autocorrelation interferogram is used to find timing between the two 3 μm pulses as well as to obtain the spectrum of the pulses using Fourier transform. These 3 μm pulses are temporally characterized by interferometric autocorrelation using a second harmonic generation in an AgGaS₂ crystal.

The other output of the amplifier is sent to the BBIR setup with 1.0-1.5 mJ/pulse energy. This 800 nm input goes through a delay stage that controls the time delay between 3 μm and BBIR pulses. A transmissive telescope shrinks the 800 nm beam from ~15 mm to ~9 mm, so as to comfortably pass it through the nonlinear crystals (10 sq. mm size of the crystals) used in the BBIR generation process. The fundamental, second and third harmonic of the 800 nm pulses are focused in dry air using a spherical dielectric mirror to generate a plasma, which acts as a source for the BBIR. The resultant BBIR beam is then collimated and expanded to a size of ~15 mm using a reflective telescope in order to focus tighter on the sample. After its expansion, the BBIR beam is passed through a high resistivity Si wafer placed at Brewster’s angle. It filters out wavelengths <1.1 μm from the BBIR pulses. On this wafer, we spatially overlap the BBIR with a HeNe tracer beam for alignment purposes.

The 3 μm and BBIR pulses propagate parallel to each other but at different heights, with a vertical separation of 1”. They are focused onto the sample using an off-axis bare
gold parabolic mirror (Janos Tech). All the 2DIR and TA experiments shown in thesis are performed in the pump-probe geometry. In this geometry, the third order nonlinear signal travels along the probe (BBIR pulse in our case). After passing through the sample, all the pulses are collimated using an identical off-axis bare gold parabolic mirror. Subsequently, only the BBIR pulse and the co-propagating third order nonlinear signal is dispersed onto a liquid N\textsubscript{2} cooled MCT array detector for spectral detection (Infrared Systems).

### 3.3. Generation and Characterization of 3\textmu m Pulses:

Sub-45 fs 3\textmu m pulses are generated using a home-built BBO-K\textsubscript{NbO}\textsubscript{3} OPA, pumped by 600 mW of the sub-25 fs 800 nm output of a commercial Ti:sapphire amplifier. The detail design of the OPA is described in [19], therefore only a brief description is presented here. An AR coated fused silica window reflects ~1% of the input 800 nm pulse that is focused onto a sapphire plate using a spherical concave mirror to generate a white light continuum. A \(\lambda/2\) waveplate and thin-film polarizer combination controls the power of 800 nm pulse into the white light generation process. After collimation by a spherical mirror, the white light continuum is focused on a Type I BBO crystal cut at \(\theta = 29.2^\circ\) and \(\phi = 0^\circ\) (Casix), using a fused silica convex lens. ~37% of the remaining 800 nm pulse is sent to a translation stage before focusing on the same BBO crystal. Spatially and temporally overlapped white light continuum and 800 nm pulses on the BBO crystal generate 1.1 \textmu m signal and 3 \textmu m idler, however, the idler is absorbed by BBO. A custom dichroic mirror (Cascade Optical) subsequently reflects only the 1.1 \textmu m signal onto the K\textsubscript{NbO}\textsubscript{3} crystal, transmitting the 800 nm light.

The remaining part of 800 nm pulse is sent to a translation stage after shrinking its
size by transmitting through a transmissive fused silica telescope. Thereafter, it is spatially and temporally overlapped with the 1.1 μm signal out of BBO on a 1 mm thick KNbO3 crystal (Type II, Spectrogen Inc.). The 800 nm and 1.1 μm pulses generate 3 μm pulses, which is not absorbed by KNbO3. Due to the small thickness of the KNbO3 crystal, it can minimize dispersion of the 3 μm pulses. Residual 800 nm light is removed from the 3 μm pulses using an 800 nm high reflector and is subsequently collimated to a size of ~10 mm, using a CaF2 transmissive telescope. A 2 mm thick AR coated Ge window, placed at Brewster’s angle, removes any residual visible and near-IR from the 3 μm pulses. Apart from that, Ge introduces positive second order dispersion to the 3 μm pulses which pre-compensates for the negative second order dispersion introduced by the CaF2 beamsplitters in the interferometer [21]. Any additional second order dispersion can be compensated by using a thin ZnSe or CaF2 window along the beam path, which introduces positive and negative second order dispersions, respectively. Overall, the 3 μm pulses generated in this OPA have an average power of ~4-5 μJ/pulse and are linearly polarized.

After generation, the 3 μm pulses are spatially overlapped with a HeNe tracer beam on the Ge window mentioned above, for alignment purposes. A flipper mirror placed right before the entrance of the interferometer jogs both the beams for a long distance (~3 meters) to a far field detector. Two mirrors are placed right before the Ge window, to overlap the 3 μm pulses onto to the HeNe in both near and far field.

After HeNe overlap, the 3 μm pulses are sent to a Mach-Zehnder interferometer for generation of collinearly propagating time ordered pulse pairs. One of the pairs is sent to a room temperature MCT detector to get a field autocorrelation of the pulses, as shown in Fig. 3-3A. The interferogram of field autocorrelation helps us find timing between the two
3 μm pulses in the pair. Alongside, Fourier transform of the interferogram provides us with the spectrum of the pulses, shown in Fig. 3-3B. The peak frequency of the pulse can be tuned in the 3000-3500 cm⁻¹ region by rotating the angle of the KNbO₃ crystal and compensating for temporal walk-off by moving the translation stage used by last fraction of the 800 nm input pulse. On the other hand, bandwidth of the OPA output is sensitive to the angle of the BBO crystal and it provides a FWHM bandwidth of ~400 cm⁻¹ [19].

**Figure 3-3:** (A) Field autocorrelation of 3 μm pulses. The maximum of the interferogram corresponds to perfect time overlap between the pulses within a pair generated by the interferometer. (B) Fourier transform of the field autocorrelation interferogram yields the spectrum of the 3 μm pulses. The center of the spectrum can be tuned in the ~3000-3500 cm⁻¹ region reproducibly, by changing the angle of KNbO₃ crystal.

For temporal characterization of the 3 μm pulses, we perform interferometric autocorrelation using second harmonic generation process. For this purpose, we use a 3 μm pulse pair and focus them onto a 300 μm thick Type I AgGaS₂ crystal (cut at θ = 37.4° and φ = 45°), using bare gold off-axis parabolic mirrors. The time delay between the pulses is
scanned by moving one arm of the interferometer. The resulting second harmonic of the 3 μm is sent into an InGaAs photodiode (Thorlabs). The resulting interferometric autocorrelation, shown in Figure 3-4, is fitted to a Gaussian envelope to extract 42 fs FWHM width for the 3 μm pulses.

![Figure 3-4: Interferometric autocorrelation of 3 μm pulses using a second harmonic generation using an AgGaS₂ crystal. A Gaussian envelope fit yields 42 fs FWHM width of the pulses.](image)

3.4. Generation and Characterization of BBIR pulses:

3.4.1. Generation of BBIR Pulses:

With the development and increased availability of Ti:sapphire amplifiers that generate 800 nm pulses with temporal widths of <25 to 100 fs, a lot of effort has gone into generation of broadband optical pulses, with FWHM bandwidth >1000 cm⁻¹ [20,22–35]. These pulses, generated in various regions of frequencies starting from ultraviolet to terahertz, usually have temporal widths of 50-100 fs. Thus, they can be used in ultrafast spectroscopy experiments. Implementation of BBIR pulses in ultrafast spectroscopy is a
very recent development and our group is the first one to successfully achieve that [36–39].

Generation of broadband optical pulses employ a different strategy compared to that of OPA. In contrast to OPA, no difference frequency generation or down-conversion of optical pulses in nonlinear crystals is involved in this process. Instead, ultrashort 800 nm pulses and its harmonics are focused in a gaseous medium to generate a plasma, which subsequently acts as a source for the broadband optical pulses. Focusing of ultrashort optical pulses in a gaseous medium leads to a phenomenon called “filamentation”. Filamentation involves two opposing effects involving focusing of short laser pulses. Due to high peak power of these pulses, strength of electric field near the focus of the beam is very high. This result a high intensity dependent refractive index in a gaseous medium near the focus, causing the beams to self-focus. On the other hand, the plasma created at the focus is of low density, with an opposing defocusing effect to the beams. As a result, there are formation of multiple foci in the direction of propagation of the input beams near the focus. Such an effect produces an elongated focus and provides a larger interaction length for the focusing beams leading to generation of efficient broadband pulses [40].

The exact mechanism for the generation of these broadband pulses from the plasma is uncertain. There are two major explanations provided in the literature. One of arguments put forward tunneling ionization process in a gaseous medium, caused by focusing fundamental and harmonics of ultrashort 800 nm pulses, to be responsible for generation of broadband pulses, particularly in terahertz domain [41]. It suggests that an asymmetry is created in tunnel ionization due to use of two different frequencies of optical inputs. Interference between two ionization pathways resulted by them causes an electron current
which emits broadband pulses. On the other hand, a four wave mixing process in a gaseous medium is proposed to be an alternative explanation for generation of BBIR and terahertz pulses based on input power dependence studies [23,25,27,34,35]. Here, third order nonlinear susceptibility of the gas medium is proposed to be responsible for successful generation of the broadband pulses. While the peak frequencies in a four wave mixing process add up to zero, broadband IR and terahertz pulses are generated due to finite bandwidth of the input pulses. While a mechanistic study of broadband pulse generation is an important problem in its own right; in this thesis, I have focused on generation, characterization and use ultrashort BBIR pulses in nonlinear IR spectroscopy.

Generation of broadband mid-IR pulses is heavily influenced by broadband terahertz pulse generation. Most of the procedures used sub-25 fs 800 nm and its second harmonic (400 nm) pulses as inputs in the generation process [29,35]. Individual procedures vary on the basis of geometry of second harmonic generation (collinear or non-collinear), use of shorter or longer focal length optic for focusing the beams, choice of gaseous medium to generate the plasma and some other factors. We have adopted the method used by Petersen and Tokmakoff for generation and subsequent use of BBIR pulses in nonlinear spectroscopy [20].

In this method, we add the third harmonic of sub-25 fs 800 nm pulses along with its fundamental and second harmonic for BBIR generation. The second and third harmonic are generated collinearly, as shown in Fig. 3-5. First, sub-25 fs 800 nm pulses with 1.0-1.5 mJ/pulse energy are sent through a 0.2 mm thick Type I BBO crystal (cut at 29.2°) for the generation of 400 nm pulses. A 2 mm thick BBO crystal (cut at 66°) is subsequently used as a delay plate that compensates for the temporal walk-off between the 800 and 400 nm
Figure 3-5: Setup for generation of BBIR pulses using fundamental, second and third harmonics of sub-25 fs 800 nm pulses. $2v =$ doubling crystal, DP = delay plate, WP = dual waveplate and $3v =$ tripling crystal.

pulses. As the 400 nm pulses are generated in a type I process, its polarization is perpendicular to that of 800 nm pulse (P-polarized 400 nm and S-polarized 800 nm). A dual waveplate, 6.5$\lambda$ at 800 nm and 14$\lambda$ at 400 nm, rotates the polarization of 800 nm onto that of 400 nm pulse. These collinearly propagating 800 nm and 400 nm pulses are then sent through another 0.1 mm thick type I BBO crystal, cut at 44.26°, to generate the 267 nm pulse. Addition of third harmonic improves the overall intensity of the resulting BBIR pulses by a factor of $\sim$10 along with increasing intensity in the >3000 cm$^{-1}$ spectral region. At the same time, without the third harmonic, the BBIR pulses are elliptically polarized as opposed to being linearly polarized with its inclusion [20]. Intensity of the resulting BBIR pulses are optimized by varying the compression of input 800 nm pulses; angles of the doubling crystal, delay plate and the tripling crystal; and setting of the dual waveplate,
without any particular order. Few iterations involving the above degrees of freedom are required to find the global intensity maxima for BBIR pulses.

The collinearly propagating 800 nm, 400 nm and 267 nm pulses are focused in dry air using a spherical dielectric mirror of 5 cm focal length to create a plasma. The dielectric mirror is coated for 800 nm and 400 nm light, but also has a high reflectivity for 267 nm light. Other groups have used longer focal length spherical mirrors (50-400 cm focal length) to focus the pulses that generate the plasma [33–35]. In order to reduce distortion of the plasma and the generated BBIR, the angle of incidence on the spherical mirror should be as close to 0° as possible. From that perspective a longer focal length spherical mirror is a preferred option. However, our choice of shorter focal length spherical mirror is primarily based on observed ~10 fold gain in overall intensity of the BBIR pulses compared to a longer focal length mirror. This gain in intensity might as well arise from the fact that the shorter focal length mirror had a dielectric coating with 99% reflectivity of the pulses as opposed to ~85% reflectivity of a longer focal length metallic mirror. Apart from boost in overall intensity, the use of shorter focal length mirror provides more intensity of the BBIR pulse in >3000 cm⁻¹ spectral region, essential to probe the O—H stretch vibrations in aqueous solutions.

The BBIR pulses generated from the plasma are collimated using a spherical UV enhanced silver mirror of 5 cm focal length. After collimation, the BBIR pulses propagate along the same direction as the visible pulses with a slight vertical displacement. We can partially remove the visible pulses by placing an iris in the beam path. The rest of the visible pulses and pulses with wavelength below 1.1 μm are removed by placing a 400 μm thick high resistivity (>1000 Ω.cm) Si wafer (MTI Corporation) at Brewster’s angle (~70°) along
the beam path. A HeNe tracer beam is spatially overlapped with the BBIR on this Si wafer for help in alignment. For this purpose, the BBIR along with the HeNe is sent to a far-field liquid N$_2$ cooled single channel MCT detector that measures the intensity of the BBIR pulses integrated across its bandwidth. The BBIR beam is overlapped onto the HeNe beam in near and far field by using two plane gold mirrors placed before the Si wafer.

3.4.2. Spectral Characterization:

![Spectrum](image)

*Figure 3-6: Spectrum of the BBIR pulses detected using a 64 element liquid N$_2$ cooled MCT array detector, with a 6 μm blazed 50 grooves/mm grating. The feature at ~2350 cm$^{-1}$, indicated by the green arrow, is due to atmospheric CO$_2$. Interference from atmospheric water is also observed in the 3600-3700 cm$^{-1}$ and 1500-1800 cm$^{-1}$ regions of spectrum, as indicated by the blue arrows.*

For spectral detection of the BBIR pulses, it is dispersed on a 64 element liquid N$_2$ cooled MCT array detector. Figure 3-6 shows the spectrum of the BBIR pulse, ranging from ~1000 cm$^{-1}$ to 4000 cm$^{-1}$. The detector response dies off in the lower frequencies
producing a tail in the low frequency region [20]. The intensity at higher frequencies, however, can be varied by rotating the delay plate and the tripling crystal about the vertical axis, and by tuning the compression of the 800 nm pulses. These optimizations help to generate a higher energy plasma, conducive for generation of higher frequencies. Due to large bandwidth of the BBIR pulses, we need to disperse different regions of the spectrum separately and stitch them together to get the entire spectrum, as discussed in detail in section 3.5.

![Graph](image)

**Figure 3-7:** Dependence of input power of 800 nm pulses on overall intensity of the BBIR, i.e. integrated intensity across the spectrum. The BBIR intensity has been normalized to the maximum intensity obtained across all input powers.

Overall intensity of the BBIR pulses is dependent on the input power of the 800 nm pulses. The BBIR intensity grows with increase in input power up to ~1.15W and decreases beyond that, as shown in Fig. 3-7. Our use of a short focal spherical mirror to focus the 800 nm, 400 nm and 267 nm pulses make the plasma very confined and with high energy density. Increase in input power beyond a certain point increases noise and makes the
resulting BBIR unstable. However, the threshold input power of 800 nm pulses for maximum BBIR output also depends on its spectrum. When the spectrum contains less of higher frequencies, unlike in Fig. 3-6, the threshold is slightly higher [42].

3.4.3 Polarization of BBIR pulses:

![Figure 3-8](image)

*Figure 3-8:* Spectrum of the BBIR pulses at different polarization angles. (A) All the spectra are normalized to the maximum intensity of BBIR when the polarizer is placed at 0° with respect to the BBIR polarization. (B) All the spectra are normalized to their own maximum intensity.

The BBIR pulses generated using the method mentioned above are linearly polarized in the 1000-4000 cm\(^{-1}\) region, rotated about ~16° from the vertical axis. In order to study the polarization characteristics of the BBIR pulses, we send it to the MCT array detector through a polarizer. Figure 3-8A shows that the intensity of the BBIR pulses is diminished with rotation of the polarizer and eventually almost extinguished when it is rotated by 90°. However, the spectrum of the BBIR pulses do not change much with
rotation of the polarizer, indicating the same polarization across the spectrum (Fig. 3-8B).

3.4.4. Temporal Characterization of BBIR Pulses:

![Graph showing time delay vs. BBIR bleach](image)

**Figure 3-9:** (Red circles) Step response obtained due to cross-correlation of BBIR pulses with temporally characterized sub-45 fs 3 µm pulses out of the OPA. The step response is fit to an error function (blue trace) to obtain temporal width of <70 fs for the BBIR pulses, assuming response of the material to be faster than the pulse duration.

In order to determine the temporal width of the BBIR pulses, we measure cross-correlation of these pulses with temporally characterized sub-45 fs 3 µm pulses out of our OPA. The cross-correlation is performed on a 500 µm thick InSb wafer, whose band gap is ~7.3 µm. Due to its low band gap, both the 3 µm and BBIR pulses cause above band gap transitions in InSb. However, owing to much larger intensity of the 3 µm pulses, it acts as a pump and is responsible for a much stronger transition. By varying the time delay between the 3 µm and the BBIR pulses, we obtain a step response curve, as the carriers generated by the pulses are longer lived than the pulse duration (Fig. 3-9). In order to
estimate the temporal width of the BBIR pulses, we fit the step response to an error function (Fig. 3-9). The fit yields a \( \sim 70 \) fs temporal width for the BBIR pulses, similar to pulses generated by other groups [29,33–35]. Due to finite thickness of the InSb wafer, the measured cross-correlation might yield a larger value for the pulse width than it actually is. Therefore, we use the result of the measurement as an upper bound to the BBIR pulse width. Even with this consideration, the BBIR pulses are longer compared to what is expected for a pulse of similar bandwidth. It is likely that the plasma does affect the pulse width somewhat due to dispersion effects along with the Si wafer, which introduces a positive second order dispersion across the spectrum.

On the other hand, temporal chirp is a concern for pulses with as large a bandwidth as the BBIR. In order to characterize the temporal chirp, we have performed cross-correlation of the BBIR and sub-45 fs 3 \( \mu \)m pulses out of the OPA on a 1 mm thick CaF\(_2\) window. Figure 3-10 shows the resulting signal dispersed on the MCT array detector as a function of time delay between the pulses. From this measurement, we find a linear temporal chirp of \( \sim 80 \) fs in the BBIR pulses between 1350 cm\(^{-1}\) and 4000 cm\(^{-1}\). The cross-correlation measured in this method is also \( \sim 70 \) fs, similar to what we measured on an InSb wafer. We haven’t found much difference in the temporal characteristics of the BBIR pulses as we changed its spectrum, similar to the results of Petersen and Tokmakoff [20].
3.5. Measurement of Nonlinear Infrared Signals:

The ultrafast IR pulses generated using the methods described in the last two sections are used to perform 2DIR and TA experiments on neat water and aqueous hydroxide solutions. 2DIR spectroscopy uses three time ordered mid-IR pulses to sequentially excite the system that drive the emission of resonant third order nonlinear signal. The first pulse creates a coherent superposition of two vibrational states; after a time delay $\tau_1$, a second pulse breaks the coherence; subsequently, after a time delay $\tau_2$, a third pulse recreates a coherence between two vibrational states that lasts for a time $\tau_3$, before
the signal is emitted in a phase-matched direction [43,44]. For obtaining absorptive 2DIR spectrum, we need both the amplitude and phase of the signal. For that purpose, the signal is interfered with another pulse, a process known as heterodyning. The heterodyned signal is thereafter detected on an MCT array detector resulting the detection frequency ($\omega_3$) axis of a 2DIR spectrum. On the other hand, Fourier transform of the oscillations in $\tau_1$ provide the excitation frequency ($\omega_1$) axis of the spectrum. Finally, we obtain 2DIR spectra as a function of waiting time $\tau_2$.

Such a 2DIR spectrum can be interpreted as probability of exciting a vibration at a given frequency $\omega_1$ and detecting it at another frequency, $\omega_3$, after a waiting time $\tau_2$. In contrast, TA spectra are essentially 2DIR surfaces integrated across the $\omega_1$ dimension. They are obtained when the first two interactions are coincident, i.e. $\tau_1$ is zero. Although it loses resolution along the excitation frequency axis, we can easily generate TA spectra for many waiting times, $\tau_2$, unlike 2DIR spectra. Therefore, in studying dynamics as a function of waiting time ($\tau_2$) TA is a useful technique.

The first two pulses that interact with the sample in 2DIR or TA experiments are called pump pulses and the third pulse is called the probe pulse. The pump pulses need to be much more intense compared to the probe pulse. Intensity of our BBIR pulses are not enough to be used as pump in 2DIR or TA experiments. However, it has enough intensity to be used as a probe. All the experimental spectra shown in this thesis uses sub-45 fs 3 $\mu$m pulses out of the OPA as pump and the BBIR pulses as probe. As a result, the 2DIR spectra obtained in this method has a much broader $\omega_3$ axis compared to the $\omega_1$ axis, which we distinguish as broadband 2DIR (BB 2DIR) spectra.
The BB 2DIR experiments are performed in pump-probe beam geometry. In this geometry, the two time ordered pump pulses propagate collinearly as shown in Fig. 3-11 and the probe pulse comes at an angle. The rephasing and non-rephasing third order nonlinear signal is emitted in a phase-matched direction that is coincident with the probe pulse. The probe pulse also heterodynes the third order nonlinear signal in this geometry. Switching from BB 2DIR spectroscopy to TA spectroscopy in the pump-probe geometry can be done by blocking one of the pump pulses and scanning the other pump pulse with respect to the probe in time. The TA signal co-propagates along the probe and is detected by dispersing it onto the MCT array detector.

For BB 2DIR experiments, we generate time ordered pulse pairs of sub-45 fs 3 μm pulses out using a Mach-Zehnder interferometer, as shown in Fig. 3-12. First, a 3 mm thick 50/50 CaF₂ beamsplitter (BS1, anti-reflection coated for 3 μm on one side and beamsplitter coated on the other) splits the 3 μm output from the OPA into two arms. One of the arms is sent to a retro-reflector mounted on a motorized translation stage (Aerotech). This translation stage scans the delay between the two arms and constitutes the τ₁ dimension. The other arm is sent to another retro-reflector that is kept fixed. The fixed arm of the
Figure 3-12: Experimental setup for BB 2DIR spectroscopy. L1 and L2 are fused silica lenses for telescoping down 800 nm beam. 2v = doubling crystal, DP = delay plate, WP = dual waveplate and 3v = tripling crystal. FM is a dielectric focusing mirror with f = 5 cm coated for 800 nm and 400 nm; CM is a collimating mirror with UV enhanced silver coating with f = 5 cm; SM1 and SM2 are spherical gold mirrors with f = -10 cm and +25 cm, respectively for enlarging the BBIR beam. BS1 and BS2 are 50/50 CaF2 beamsplitters; WP is a λ/2 waveplate; P1 and P2 are MgF2 wire-grid polarizers and C is a chopper. PM1 and PM2 are 3” bare gold off-axis parabolic mirrors with effective focal length of 10.16 cm; PM3 is a 2” off-axis gold parabolic mirror with an effective focal length of 20 cm; S is sample. The filled black circles represent periscopes.
interferometer is chopped at half the laser repetition rate (500 Hz). Both the beams were then spatially re-combined on a similar 50/50 beamsplitter (BS2). This recombination generates two pulse pairs propagating perpendicular to each other. One of them is sent through a waveplate (WP) and a wire-grid polarizer (P1, MgF2) in order to control the polarization of the 3 μm pulse pair with respect to the polarization of the BBIR pulses. The other pulse pair is sent to a room temperature MCT detector to generate the field autocorrelation of the pulses. It enables us to time them up along with calculation of 3 μm pulse spectrum by Fourier transforming the field autocorrelation interferogram.

The excitation frequency axis (ω₁) of a BB 2DIR spectrum is obtained by Fourier transforming the time delay between the two pump pulses (τ₁). Movement of the motorized translation stage that measures the time delay between the two pump pulses, is controlled by an encoder. Often the stage needs to be stopped at a point between two marks on the encoder, which is determined by interpolation. Inaccuracies in this interpolation due to round-off or other complicating factors can lead to systematic step size errors. Therefore, even though the stage motion is reproducible within ~50 nm (0.167 fs), we have an error in timing. Errors in stage position or timing result mixing of the real and imaginary parts of the BB 2DIR spectrum, causing distortions to the absorptive BB 2DIR lineshape. The systematic errors in the stage position can be corrected by interferometric calibration. An accurate calibration is done by HeNe quadrature detection using the HeNe beams co-propagating with the 3 μm pulse pair [45,46]. We place a λ/2 waveplate in one arm of the interferometer and a λ/4 waveplate in the other. The λ/2 waveplate generates linearly polarized light whereas the λ/4 one creates circularly polarized light. One of the outputs of the interferometer is used after the beams are re-combined on the combining beamsplitter.
Figure 3-13: (A) Timing error extracted by interferometric calibration of the translation stage using HeNe quadrature detection. Periodicity in the error suggests its systematic nature, caused largely due to the encoder. (B) Fourier transform of a HeNe interferogram obtained before and after applying the correction. There are numerous side bands in the uncorrected spectrum, whereas, there is only a sharp peak at 632.8 nm after calibration.

(BS2). The output is sent through a beam cube to separate S and P polarizations, which are subsequently sent to two identical photodiodes (Thorlabs DET210). By moving the translation stage, a HeNe interferogram is measured on the photodiodes. The angle of the λ/2 wave plate is adjusted to ensure that the fringe depth measured by both detectors is equal. The interferograms at S and P polarization are π/2 out-of-phase with each other. The inverse tangent of the ratio of P and S polarization interferograms results in the phase accumulated due to movement of the stage. Subsequently, the error in timing can be calculated from the following expression [47]:

\[ dt = \frac{\lambda_{\text{HeNe}}}{4\pi c} \, d\phi \]  

(3-1)

Here, \( \lambda_{\text{HeNe}} \) is the wavelength of the HeNe laser, which is 632.8 nm, \( c \) is the speed of light and \( d\phi \) is the accumulated phase error. A look up table is constructed with finely spaced...
stage positions and their corresponding errors. Thus, the accurate positions of the stage and the corresponding accurate time delays are always obtained during data acquisition.

Time delay between the pump pulses and the BBIR probe pulse ($\tau_2$) is controlled using a delay stage (Aerotech) that delays the 800 nm pulses into the BBIR generation setup. A transmissive telescope (L1 and L2 in Fig. 3-12) shrinks the input 800 nm beam to a size of ~9 mm to avoid getting clipped on the nonlinear crystals. After the generation of the BBIR pulses from the plasma and its subsequent collimation, size of this beam is increased from ~7 mm to ~15 mm using a reflective telescope (SM1 = −10 cm FL and SM2 = +25 cm FL, Fig. 3-12) constituted of spherical gold mirrors. The BBIR beam is then spatially overlapped with a HeNe tracer beam on the Si wafer, to help with subsequent alignment.

The 3 μm and the BBIR beams travel parallel to each other but vertically displaced by an inch. They are focused onto the sample using a 3” diameter off-axis bare gold parabolic mirror, with a reflective effective focal length of 10.16 cm (PM1, Fig. 3-12). After passing through the sample, the beams are collimated using an identical bare gold off-axis parabolic mirror (PM2, Fig. 3-12). An iris is placed after the collimating parabolic to block the 3 μm pulses and let through the resonant signal, co-propagating along the BBIR pulses. This prevents scatter from the pump pulses to getting into the array detector. We place an analyzing polarizer (P2, Fig. 3-12) soon after the sample. Its angle is set at a value where maximum BBIR intensity is transmitted through the polarizer.

At the focus, the size of the 3 μm and BBIR beams are ~120 μm and ~200 μm, respectively. These sizes are determined by placing a 100 μm pinhole at the focus and measuring ~80% and ~50% transmission through it for the 3 μm and BBIR beams,
respectively. The 3 \( \mu \)m and BBIR pulses are timed up using the cross-correlation on an InSb wafer placed at the focus. For more accurate timing of the pulses, we place a 50 \( \mu \)m pinhole at the focus of the beams and measure the cross-correlation from the scattering of the pinhole. The scattered light is sent to the MCT array. By moving the \( \tau_2 \) stage, we generate an interferogram of the cross-correlation that is used to find timing (Fig. 3-14). Since the interference between any two pulses require spectral overlap, in addition to spatial and temporal overlap, the interferometric cross-correlation accurately times up only the high frequency region of the BBIR spectrum around 3 \( \mu \)m. The BBIR pulse has a temporal chirp of \( \sim 70 \) fs in the 1350-4000 cm\(^{-1}\) region (Fig. 3-10). As a result, the time delay between the 3 \( \mu \)m pulses and lower frequency region of the BBIR pulse would be less than what is measured in the cross-correlation.

![Cross-correlation of the high frequency region of the BBIR pulse and the 3 \( \mu \)m pulse, obtained from scattering of a 50 \( \mu \)m pinhole.](image)

**Figure 3-14:** Cross-correlation of the high frequency region of the BBIR pulse and the 3 \( \mu \)m pulse, obtained from scattering of a 50 \( \mu \)m pinhole.
The BB 2DIR signal, co-propagating with the BBIR probe pulse, is focused onto a spectrometer equipped with a 50 grooves/mm grating blazed at 6 μm (Jobin Yvon Horiba Triax 190) using a 2” off-axis gold parabolic mirror (PM3; effective focal length ~20 cm, Fig. 3-12). The grating spectrally disperses the input beams onto a liquid N2 cooled 64 element MCT array detector to generate the $\omega_3$ dimension of the BB 2DIR spectrum. The signal in pump-probe geometry is heterodyned by the probe pulse itself. Thus, the array detects an overall intensity ($I(\omega_3, \tau_1, \tau_2)$) of the two interfering pulses, as described in Eq. 3-2.

$$I(\omega_3, \tau_1, \tau_2) = \left| E_{\text{Sig}}(\omega_3, \tau_1, \tau_2) + E_{\text{Pr}}(\omega_3, \tau_1, \tau_2) \right|^2 = \left| E_{\text{Sig}}(\omega_3, \tau_1, \tau_2) \right|^2 + \left| E_{\text{Pr}}(\omega_3, \tau_1, \tau_2) \right|^2 + 2\left| E_{\text{Sig}}(\omega_3, \tau_1, \tau_2) \right|\left| E_{\text{Pr}}(\omega_3, \tau_1, \tau_2) \right|\cos(\phi_{\text{Sig}} - \phi_{\text{Pr}})$$ (3-2)

The intensity component $\left| E_{\text{Sig}}(\omega_3, \tau_1, \tau_2) \right|^2$ is much smaller than $\left| E_{\text{Pr}}(\omega_3, \tau_1, \tau_2) \right|^2$ and hence can be neglected. We can remove the $\left| E_{\text{Pr}}(\omega_3, \tau_1, \tau_2) \right|^2$ term by using an optical chopper that chops every alternate shots of one of the pump pulses. A difference of the detected intensities for two consecutive shots would serve the purpose when both of them are taken at the same $\tau_1$ and $\tau_2$. The intensity detected on the array is therefore related to the cosine of the difference between the phase of the signal ($\phi_{\text{Sig}}$) and that of the probe ($\phi_{\text{Pr}}$) (also known as local oscillator). An accurate determination of these phases is crucial to obtain artifact free absorptive BB 2DIR spectrum. Since the signal in the pump-probe geometry is inherently timed up with the probe pulse/local oscillator, errors in $\tau_3$ timing are absent in this measurement, i.e. measurement of these phases is always accurate. However, the local oscillator/probe intensity cannot be controlled independently of the signal intensity in this geometry. Both the probe and signal intensity needs to be attenuated
after the sample in order to be within the saturation threshold of the array detector. Therefore, for systems with very low third-order signal, the pump-probe geometry would result in lower signal-to-noise. Since measuring distortion free BB 2DIR lineshapes of aqueous systems are our priority, we employ the pump-probe geometry for BB 2DIR data acquisition.

**Figure 3-15:** (A) Field autocorrelation of 3 μm pulses (left) and its Fourier transform (right) before and after correcting for the time overlap of the pulses. The timing error in this case is 1 fs. (B) Stitched BB 2DIR spectra of H₂O at τ₂=100 fs. The solid black lines along ω₁ marks different grating positions. The spectral region below 2400 cm⁻¹ in ω₃ is multiplied by a factor of 10. The asterisk marks the region of spectral interference by atmospheric CO₂.

For BB 2DIR experiments, we scan the τ₁ axis from -100 fs to 400 fs in steps of 2 fs (frequency resolution of 83 cm⁻¹). The time delays are subsequently Fourier transformed
to obtain the excitation frequency axis, \( \omega_1 \). Inaccuracy in timing between the first two pulses (\( \tau_1 \)) is corrected during data processing by adding a constant phase factor along the \( \omega_1 \) dimension (\( e^{i\Delta \tau_1} \)), since any errors in the pulse timings can distort the 2DIR lineshape by introducing artifacts. We simultaneously collect the field autocorrelation interferogram of the 3 \( \mu \)m pulses to find timing errors in \( \tau_1 \). Fourier transform of this interferogram is real when the pulses are perfectly timed up. We shift the interferogram in time to obtain a Fourier transform with minimum imaginary component, usually within \( \pm 10 \) fs (Fig. 3-15A). The amount of shift is the error in \( \tau_1 \) timing.

We express the measured third order nonlinear signal on the array detector as a change in absorbance, \( \Delta OD = -\log \left( \frac{I_{\text{open}}}{I_{\text{close}}} \right) \), where \( I_{\text{open}} \) is the intensity measured on the detector when all the pump and probe pulses interact with the sample and \( I_{\text{close}} \) is the intensity when one of the pump pulses is chopped at half the laser repetition rate. Owing to its large bandwidth of the BBIR pulse, we use few different grating positions to detect different regions of frequency, with a little bit of overlap between two consecutive grating positions. During post-processing of the data, results of different grating positions are stitched together to obtain the entire spectrum. In order to avoid artifacts due to higher order dispersion of the grating, we place a long pass filter while detecting the spectral region below 2200 cm\(^{-1}\). Figure 3-16B shows a BB 2DIR spectra of H\(_2\)O at \( \tau_2 = 100 \) fs, where the spectra is collected using four different grating positions to construct the \( \omega_3 \) axis.

3.6. Summary:

The methods described in this chapter are used to collect BB 2DIR and TA spectra
of neat liquid water and aqueous hydroxide solutions, as shown in chapters 4 and 6. Our ability to generate BBIR pulses and its implementation in ultrafast nonlinear IR spectroscopy has made it possible to explore complex vibrational coupling and dynamics present in this system.

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References:


Chapter 4

Collective Vibrations of Water-Solvated Hydroxide Ions Investigated with Broadband 2DIR Spectroscopy

4.1. Introduction:

Proton transport in aqueous solution is at the heart of acid-base and redox chemistry [1–5], yet it is difficult to gain molecular insight into this process by experimental methods. The textbook picture of proton transport in water, based on von Grotthuss’s proposal [6], argues that proton transport is translocation of the ion by shifting a proton to its neighbor along hydrogen bonds of water, rather than Brownian diffusion. While this basic picture is generally accepted for transfer of an excess proton, it is not often appreciated that a similar process occurs in hydroxide solutions, through proton transfer from water to the OH\(^-\) ion. The proton transfer process remains difficult to describe in both cases, since the solvated structure of the ion and the dynamics of three dimensional hydrogen bonding network of water molecules are intimately intertwined in the process.

In numerous theoretical and experimental studies, proton transfer in aqueous hydroxide is described in terms of the interconversion of coordination structures of solvated OH\(^-\) ion complex [7–20], a concept analogous to interchange between Eigen and
Zundel species of the excess proton. One picture proposes the solvated OH\(^-\) complex to be a 3-coordinate H\(_7\)O\(_4\)\(^-\) species in its most stable form, where the OH\(^-\) ion accepts three hydrogen bonds from water and donates none [7,10–12]. During proton transfer, the proton becomes equally shared between two OH moieties giving rise to an intermediate H\(_3\)O\(_2\)\(^-\) species. The 3-coordinate stable structure of solvated OH\(^-\) ion is supported by gas-phase IR spectroscopy of OH\(^-\)(H\(_2\)O)\(_n\) (n = 1–5) clusters [21,22]. However, this mechanism is put into question by Car-Parrinello molecular dynamics (CPMD) and empirical valence bond molecular dynamics (EVB-MD) simulations, which observes a 4-coordinate stable structure of solvated OH\(^-\), wherein the OH\(^-\) ion accepts four hydrogen bonds from the surrounding water molecules and donates none [8,9,13–20]. According to this picture, the fluctuations in water structure cause the solvated OH\(^-\) ion to lose one accepting hydrogen bond and to transiently donate one in order to act as a favorable configuration for transfer of a proton from the solvation waters to the ion. Neutron scattering [23–26], x-ray diffraction [27] and absorption [28] measurements and core-level photoelectron emission experiments [29] on aqueous NaOH indicate that the average coordination number of the OH\(^-\) ion is 3.9±0.3 at concentrations less than 10M and it donates a hydrogen bond only transiently if at all, consistent with the CPMD and EVB-MD simulation results. On the other hand, recent studies have suggested an even higher coordination number for the stable solvated OH\(^-\) ion [30–32] and multiscale and multidynamical nature of proton transport in aqueous hydroxides involving a broader distribution of pathways than previously assumed [33].

However, hydrogen bonds in liquid water fluctuate on femtosecond to picosecond timescales, resulting in changes in the solvation structure of the OH\(^-\) ion. These structural
changes strongly influence the vibrations present in the system. Ultrafast infrared (IR) spectroscopy is a well-suited technique for probing the effect of hydrogen bond fluctuations on vibrational frequencies of the system, as it possesses the required time resolution of \(~50-100\) fs alongside being sensitive to changes in vibrational frequencies with changes in hydrogen bond strength [34–37]. In aqueous hydroxides, stronger hydrogen bonding of water molecules with the OH\(^-\) ion compared to that in bulk water results in dramatic redshifts of the O—H stretch vibrational frequencies of the system. It is manifested as a continuum absorption composed of massively broadened and overlapping peaks that span the mid-IR spectral region [38–41]. Describing the molecular origin of the broad absorption feature that forms this continuum provide insight into the structure and dynamics of the solvated OH\(^-\) ion.

An early assignment argues that the absorption continuum originates from H\(_3\)O\(_2\)\(^-\) species, where the proton, equally shared between two OH moieties, is in a double-well potential leading to low frequency fundamental O—H stretch transitions. At the same time the shared proton is highly polarizable and the asymmetry in potential resulted by its movement proximal to one of the OH moieties would alter the O—H stretch frequency significantly to become a continuum absorption feature [38,39]. However, ultrafast nonlinear IR experiments probing O—H stretch vibrations in NaOD in HOD/D\(_2\)O solutions provided evidence that shared-proton H\(_3\)O\(_2\)\(^-\) species exist only fleetingly (~110 fs) as a transition state during the transfer of a proton to OH\(^-\), occurring at slower rates (~3 ps) [42,43]. Though CPMD simulations indicate the continuum originates from O—H stretch vibrations of first solvation shell water molecules of the ion [16], characteristics of the vibrations remains unclear without much experimental evidence.
In parallel, it has been shown in recent computational studies that O—H stretch vibrations in isotopically pure liquid water are delocalized between 1-6 water molecules forming dynamically evolving vibrational excitons [44–46]. Effects attributed to these vibrational excitons have been observed in nonlinear IR experiments where evidence is found that inter- and intramolecular vibrations are strongly mixed in liquid water [47–50]. It is unclear how addition of OH⁻ ion influences these vibrations, perhaps acting to localize O—H stretch vibrational modes near the ion. Ultrafast vibrational and orientational relaxation studies of O—H stretch vibrations in NaOH in H₂O and NaOD in HOD/D₂O in conjunction with THz dielectric relaxation experiments indicate that water molecules in the first solvation shell of the OH⁻ ion act collectively [51,52], which is supported by femtosecond spectroscopy of the charge transfer to solvent transition in aqueous OH⁻ [53]. Thus, probing the continuum absorption in isotopically pure aqueous hydroxide solutions should provide insight into the collective nature of O—H stretch vibrations in the OH⁻ solvation shell and the extent of inter- and intramolecular vibrational mixing, in addition to the influence of local structure and dynamics of the solvated OH⁻ ion on these vibrations.

Ultrafast infrared transient absorption and 2DIR experiments provide information about the vibrational states of the system and couplings between them through the analysis of transitions and lineshapes, which are otherwise unattainable through linear spectroscopy. Development of an ultrafast broadband infrared (BBIR) source that spans from <400 cm⁻¹ to 4000 cm⁻¹ with a temporal resolution of <70 fs [54], as detailed in chapter 3, enables us to probe the entire mid-IR region. In this chapter, we focus on understanding the nature of the vibrations leading to the broad continuum absorption feature in aqueous hydroxide solutions using magic angle transient absorption (TA) and
broadband 2DIR (BB 2DIR) experiments, where we excite the O—H stretch vibrations of aqueous hydroxide solutions, and probe the response between 1350 and 3800 cm⁻¹.

As the vibrations in neat liquid water are not described well by a local mode picture, we use harmonic vibration analysis (HVA) of solvated OH⁻ clusters to assist in the assignment of the spectral features. The vibrations in liquid water or aqueous hydroxide are strongly anharmonic in character. Thus, use of HVA is only qualitative to get insight regarding the nature of the vibrations in liquid water and aqueous hydroxide solutions. The experimental and computational results indicate that the vibrations in aqueous hydroxides are delocalized and almost independent of local structure of the ion, but we can assign certain features of the continuum by considering the symmetry of these delocalized vibrations. These assignments paves the way in discussion of vibrational dynamics and its influence on proton transport in aqueous hydroxide solutions.

4.2. Methods:

4.2.1. Experimental:

A brief description of the procedures for ultrafast IR experiments are presented here which are detailed in chapter 3. For these experiments, mid-IR excitation and probe pulses are generated by two separate sources, each pumped by a 1 kHz repetition rate 25 fs Ti:sapphire regenerative amplifier. We use sub-45 fs transform-limited pulses centered around 3 μm to pump different O—H stretching frequencies and a sub-70 fs BBIR pulse to probe the entire continuum region including the O—H stretches. The 3 μm pulses are generated using a KNbO₃ optical parametric amplifier (OPA) as described in chapter 3 [55]. The OPA has a bandwidth of ~400 cm⁻¹ and its center frequency can be tuned
between 3100 and 3500 cm\(^{-1}\). For the probe pulse in these experiments, we use a BBIR plasma source [54]. The time-coincident fundamental, second, and third harmonic of the 800 nm pump pulse out of the Ti:sapphire amplifier are focused in dry air to generate plasma that radiates a BBIR pulse with frequencies ranging from <400 to 4000 cm\(^{-1}\). The BBIR beam is separated from the visible by passing through a 400 \(\mu\)m thick high-resistivity Si wafer placed at Brewster’s angle and is collimated at \(\sim 15\) mm. The BBIR pulse is temporally characterized by cross-correlation with a sub-45 fs 3 \(\mu\)m pulse which gives an instrument response time of \(\sim 70\) fs.

BB 2DIR experiments reported in this chapter are performed in the pump-probe geometry [56], where the first two interactions of the sample are with a collinearly propagating 3 \(\mu\)m pulse pair and the BBIR pulse acts as a probe. The 3 \(\mu\)m pulse pair is generated from the OPA output using a Mach-Zehnder interferometer. The fixed arm of the interferometer is mechanically chopped at half the laser repetition rate and the other arm is sent to an interferometrically calibrated translation stage. The time delay between the 3 \(\mu\)m pulses (\(\tau_1\)) is numerically Fourier transformed to obtain the excitation frequency axis \(\omega_1\). TA experiments are performed with a single 3 \(\mu\)m pulse for excitation, which is chopped for differential detection. Waiting time (\(\tau_2\)) between the pump and the probe pulses for these experiments is set by a separate delay stage that introduces a time delay into the 800 nm pulse that drives the BBIR generation process. The TA and BB 2DIR experiments reported in this chapter are performed in magic angle (angle between pump and probe pulse is \(54.7^0\)) and parallel polarization (\(ZZZZ\)) geometry respectively, unless mentioned otherwise.

To detect the BBIR pulse, we disperse it on a 64-element HgCdTe (MCT) array
detector with a lower frequency cutoff of 1350 cm\(^{-1}\). For both TA and BB 2DIR experiments, the signal is acquired for each detector element as a change in absorbance 
\[ \Delta A = -\log(I/I_0) \], where \( I \) and \( I_0 \) are the intensities of the probe pulse with and without the pump pulse(s), respectively. Due to the large bandwidth of BBIR and limited number of array pixels, we have used four grating positions to collect the entire BBIR spectrum with an overlap of at least 65 cm\(^{-1}\) between two consecutive grating positions: 1350–1645 cm\(^{-1}\), 1580–2055 cm\(^{-1}\), 1965–2745 cm\(^{-1}\) and 2535–3800 cm\(^{-1}\). To avoid higher-order diffraction effects while collecting the 1350–2055 cm\(^{-1}\) region, we place a 2200 cm\(^{-1}\) long pass filter in front of the detector. During post-processing of the data, the spectra are stitched by taking an average of the signal in the spectral overlap region between two consecutive grating positions.

The TA and BB 2DIR spectra presented in this chapter have been normalized to the absolute maximum peak intensity in the 3600–3800 cm\(^{-1}\) region at the longest waiting time (6 ps) and in the 3200–3600 cm\(^{-1}\) region of detection frequency (\( \omega_3 \)) respectively. The pump pulses vary slightly for BB 2DIR spectra of H\(_2\)O and NaOH solutions of different concentrations; however, we find that normalization of the data along \( \omega_1 \) by the pump spectrum is unreliable due to the large width of the peaks. Therefore, for uniformity, BB 2DIR spectra are first divided along the \( \omega_1 \) axis by the pump spectrum for which the data is acquired, and then multiplied by the pump spectrum used to acquire the highest concentration of NaOH (7M).

For all the experiments described in this chapter, aqueous solutions of NaOH are prepared by dissolving NaOH pellets (Mallinckrodt, \( \geq \)98% assay) in H\(_2\)O (purified by reverse osmosis to a resistance of 18 M\( \Omega \)). The FTIR spectra of aqueous hydroxide
solutions are taken using a Thermo-Nicolet 380 spectrometer in transmission mode using a CaF2 sample cell, and in attenuated total internal reflection mode using a Ge ATR cell. For all the transmission mode experiments, the sample is sandwiched without a spacer between two 1 mm thick CaF2 windows (pathlength ~2 μm) leading to an absorbance of 0.8–1.0 for the peak of the O—H stretch vibration in H2O as well as in aqueous NaOH solutions of concentrations up to 10M.

4.2.2. SVD Analysis of Experimental Spectra:

Due to the irreproducibility of the ~2 μm sample pathlength, when comparing solutions of varying viscosity, it is difficult to obtain a quantitatively accurate difference spectrum in order to distinguish the features of solvated OH− ion from those of neat water. To analyze changes to the FTIR and BB 2DIR spectra as a function of NaOH concentration, we use singular value decomposition (SVD), which linearly decomposes a concentration dependent series of spectra into weighted spectral components [57,58]. SVD decomposes the spectra \( S \) into orthogonal spectral components \( U \) and the corresponding concentration amplitudes \( V \) weighted by their singular values \( \Sigma \) as:

\[
S = U \cdot \Sigma \cdot V^T
\]

Mathematically orthogonal basis functions \( U \) and \( V \), generated using Eq. 4-1, are not necessarily physically relevant. To facilitate the physical interpretation of different spectral components and their concentration amplitudes, we perform a constrained SVD (CSVD) analysis, where the mathematically orthogonal basis functions are transformed into physically relevant basis functions. In order to do that, we first identify the minimum
number of components \( f \) required to approximate the data based on the singular values \( \Sigma \) of the components \( f = 2 \) for FTIR and \( f = 3 \) for BB 2DIR spectra respectively, Fig. 4-6C). A \( f \times f \) transformation matrix, \( W \) is then constructed to yield singular value weighted spectral components and their concentration amplitudes (Eq. 4-2), where the first spectral component of CSVD \( \tilde{U} \) is constrained to be the spectrum of pure water.

\[
S = (U_{1...f} \cdot \Sigma_{1...f} \cdot W) \cdot (W^{-1} \cdot V_{1...f}^T) = U^T \cdot V
\]

(4-2)

where, \( W \cdot W^{-1} = I \).

**4.2.3. Computational:**

As a result of their near-degeneracy and relatively strong coupling, the O—H stretching vibrations in the neat water and in hydroxide solutions are expected to be delocalized over multiple water molecules. Delocalized O—H stretch vibrations are observed in the gas-phase spectroscopy of water and \( \text{OH}^- (\text{H}_2\text{O})_n \) \( (n = 3–5) \) clusters [21], and recent studies of neat liquid water [44–48]. In order to assign experimental spectra and qualitatively characterize the nature of vibrational modes present in aqueous hydroxide solutions, we have performed HVA, i.e. normal mode analysis of aqueous \( \text{OH}^- \) clusters taken from an EVB-MD simulation trajectory provided by the Martinez group. Calculation of normal modes for \( \text{OH}^- (\text{H}_2\text{O})_n \) \( (n \leq 6) \) clusters have been reported previously [59–62], but these studies focus on explaining gas-phase spectroscopy of stable solvated hydroxide clusters. However, in the liquid phase, one needs to take into account the effect of solvent structure and configurational variation of the solvated ion. As a result, an analysis of
clusters derived from molecular dynamics simulations is helpful.

The HVA is performed on clusters of OH\textsuperscript{-} solvated by H\textsubscript{2}O molecules using DFT with the B3LYP density functional and 6-31G (d,p) basis set implemented in Q-Chem quantum chemistry software [63]. These clusters are snapshots taken from a simulated trajectory of solvated OH\textsuperscript{-} using the MS-EVB potential parameterized by Martinez and co-workers [17,18]. The simulation contains 214 H\textsubscript{2}O molecules and one NaOH molecule in the simulation box and the trajectory is 1.2 ns long with a time step of 1 fs. A 4-coordinate structure of the solvated OH\textsuperscript{-} ion is predicted for 65\% of the time and a 3-coordinate structure for 25\% of the time. Successful proton transfer events take place once every ~5 ps. We have analyzed approximately 1000 snapshots of the simulation taken every 1.25 ps along the trajectory.

To perform HVA, we select the OH\textsuperscript{-} ion and 17 water molecules closest to the ion so as to mimic the solvation structure up to its second solvation shell. The Na\textsuperscript{+} ion does not appear within the second solvation shell of the ion and is hence ignored for further calculations. Without optimizing or putting additional constraints on the structure, we calculate the single point energy of the cluster and construct a Hessian of the potential energy. Harmonic frequencies and normal modes are obtained by diagonalizing this Hessian. No scaling factor has been incorporated to account for the anharmonicity as the calculated harmonic frequencies are used for qualitative purposes only. Due to lack of optimization, we obtain imaginary frequencies for a few normal modes which are ignored for the rest of the analysis. As a check of reliability of DFT, we have also performed Hartree-Fock (HF) calculations for ~250 of these clusters using the same basis set.

In order to better represent the liquid, we only analyze the normal modes centered
on core water molecules and the OH\textsuperscript{−} ion, and neglect those localized to the cluster surface. Core vibrations are selected for analysis if the displacement of the H atoms hydrogen bonded to the OH\textsuperscript{−} ion accounted for >50% of the total displacement in a normal mode. The relative signs of these displacements are used to classify them by symmetry. Vibrations of the ion are defined as those modes for which the O—H stretch of the ion accounted for >70% of the mode displacement.

To compare the normal modes of aqueous OH\textsuperscript{−} with that of neat liquid water, we have performed the same HVA on H\textsubscript{2}O clusters as well. These clusters are taken from a classical MD trajectory of ~2000 SPC/E H\textsubscript{2}O molecules. The trajectory is 10 ps long and snapshots are taken from different parts of the simulation box every 100 fs. The normal modes are calculated for clusters of a selected H\textsubscript{2}O molecule surrounded by its 17 nearest neighbors, identically as that of OH\textsuperscript{−} clusters.

The result of HVA is presented in terms of a density of states (DOS) of the harmonic vibrations, and as an IR-intensity-weighted density of states, \( \rho(\omega) \). The DOS is a histogram of vibrational frequencies generated from the normal mode vibrations of all the analyzed clusters, \( D(\omega) = \sum \delta(\omega - \omega_i) \) where the vibrational frequencies are binned to 20 cm\(^{-1}\) intervals and plotted as a function of the bin center frequencies. To better reflect their relative contributions to an infrared absorption spectrum, \( \rho(\omega) \) is computed by weighting the DOS of the normal mode frequencies by the corresponding square of the transition dipole moment: \( \rho(\omega) \propto \sum_i |\mu_{\omega_i}|^2 \delta(\omega - \omega_i) \). We calculate the first derivative of the dipole moment vector with respect to the normal mode coordinates (\( \partial \mu / \partial \alpha_i \)), which is proportional to the transition dipole moments (\( \mu_{\omega_i} \)).
4.3. Results:

4.3.1. Experimental:

![FTIR spectra](image)

Figure 4-1: (A) FTIR spectra of H2O and aqueous NaOH solutions of concentrations ranging from 3M to 10M. The spectra are normalized to the maximum of O—H stretch peak at 3400 cm\(^{-1}\). (B) ATR FTIR difference spectrum of 10M NaOH/H2O and H2O. The green and red arrows in both (A) and (B) indicate growth of two peaks at 2850 cm\(^{-1}\) and 2000 cm\(^{-1}\) respectively, on addition of NaOH. The blue arrow in (B) indicates the loss of O—H stretch vibration of bulk-like H2O on addition of NaOH. Spectral features near 2350 cm\(^{-1}\) arise from atmospheric CO\(_2\).

Figure 4-1 shows the changes to the linear IR absorption spectrum of H2O that result on addition of NaOH. The FTIR spectrum of pure liquid H2O (Fig. 4-1A) contains three distinct features in the 1000–4000 cm\(^{-1}\) region, the O—H stretch transition at 3400
cm\(^{-1}\), the H-O-H bend vibration at 1650 cm\(^{-1}\) and a weaker combination band of H-O-H bend and libration (hindered rotation) at 2125 cm\(^{-1}\). On addition of NaOH in H\(_2\)O, a broad continuum absorption in the 1000–3000 cm\(^{-1}\) region grows with increasing NaOH concentration. The ATR FTIR difference spectrum of 10M NaOH in H\(_2\)O and pure H\(_2\)O (Fig. 4-1B) shows that this continuum consists of two broad peaks centered at 2850 cm\(^{-1}\) (~650 cm\(^{-1}\) width) and 2000 cm\(^{-1}\) (~725 cm\(^{-1}\) width), respectively [40]. The peak at 2850 cm\(^{-1}\) shows up as a distinct shoulder to the O—H stretch main band in high concentration FTIR spectra.

Figure 4-2: Comparison of (A) FTIR spectra and (B) dispersed transient absorption spectra at \(\tau_s = 100\) fs of 10M aqueous solutions of NaOH and KOH show no discernible difference in the spectral features. This implies that the features observed in the IR spectra are due to the solvated OH\(^{-}\) ion rather than any contributions from the cation. The asterisk in (B) marks the region of spectral interference by atmospheric CO\(_2\).

Additionally, we find no clear difference between the linear IR spectra and TA spectra of aqueous NaOH and KOH solutions (Fig. 4-2), indicating that the spectral features are due to the solvated OH\(^{-}\) ion. The lack of sensitivity to the Na\(^+/\)K\(^+\) ion is not
surprising given that the O—H stretch vibration is primarily sensitive to the nearest neighbors of the proton, typically the oxygens of bulk water or anions in salt solutions.

Increase in hydrogen bond strength typically leads to a redshift of the O—H stretch and blueshift of the H-O-H bend frequencies respectively. Given that the hydrogen bonds formed by the water molecules to the oxygen of the OH⁻ ion are stronger than the hydrogen bonds between water molecules in the bulk [38–41], we attribute the peak at 2850 cm⁻¹ to be associated with the O—H stretch vibrations of the water molecules directly hydrogen bonded to the oxygen of the ion (Fig. 4-1). Because of its unusual breadth and high frequency, the origin of the 2000 cm⁻¹ peak is less obvious (Fig. 4-1). Based on its blueshift relative to the water bend and the absence of other features, we believe that this resonance in some manner involves H-O-H bend vibrations of the solvating water molecules [39]. The small area of loss in the difference spectra relative to gain indicates a strong increase in transition dipole moment for the strong hydrogen bonds within the aqueous OH⁻ complex relative to bulk-like water (Fig. 4-1B). Finally, we note that the FTIR spectra of aqueous NaOH also show subtle changes at 3650 cm⁻¹ (Fig. 4-1A), which correspond to the strong sharp peak in Raman spectra assigned to the O—H stretch vibration of the OH⁻ ion [64–66].

To understand the nature of these vibrations better, we performed TA and BB 2DIR experiments. To help in describing the overlapping spectral features originating in H₂O and aqueous NaOH, we compare TA experiments with varying pump frequency. Although our pump pulses are ~400 cm⁻¹ broad, we can center it at 3400 cm⁻¹ (blue-pump) to preferentially excite the O—H stretch vibrations of bulk-like water molecules or at 3100 cm⁻¹ (red-pump) to preferentially excite the O—H stretches of water molecules solvating
the OH\textsuperscript{-} ion. The resulting changes in absorption between 1350 and 3800 cm\textsuperscript{-1} at 100 fs waiting time are shown in Fig. 4-3. The 100 fs time delay is the shortest for which we can assure no pulse-overlap effects, but is still short enough that the structure of the liquid has not significantly evolved.

As shown in Fig. 4-3A, the blue-pump TA spectrum of H\textsubscript{2}O at 100 fs has a bleach centered at 3400 cm\textsuperscript{-1} corresponding to the O–H stretch and a broad induced absorption below 3150 cm\textsuperscript{-1} that peaks at 2950 cm\textsuperscript{-1} and extends beyond our lowest detection frequency at 1350 cm\textsuperscript{-1}. A bleach feature centered at 1680 cm\textsuperscript{-1} corresponding to H-O-H bend vibrations shows up on top of this broad induced absorption indicating strong coupling between O–H stretch and H-O-H bend vibrations. On moving the center of the pump pulse spectrum to lower frequencies, the broad induced absorption intensifies somewhat, but the overall features of the spectrum remain unchanged (Fig. 4-3B). The induced absorption is peaked 450 cm\textsuperscript{-1} below the bleach and is unusually broad, suggesting an anharmonic shift of the O–H stretch is not enough to explain this. In fact, it has been argued that Fermi resonance between stretch and bend motions contribute to the bleach [47,67,68]. Additionally, the induced absorption is resulted by a transition to a doubly excited two-exciton state, as discussed in section 4.4. These results indicate that the inter- and intramolecular vibrations in liquid water are strongly coupled [49,50,69] and the vibrations are delocalized over multiple molecules [47].

On addition of NaOH, distinct differences are observed in the blue- and red-pump TA spectra. Even though the differences are observed at all NaOH concentrations, they are best distinguished at higher concentrations of NaOH. Hence, we discuss the spectral features due to solvated OH\textsuperscript{-} ion with the help of 7M NaOH solution spectra. In the blue-
Figure 4-3: Dispersed transient absorption spectra of H₂O and aqueous solutions of NaOH of concentrations ranging from 3M to 7M, taken at τ₂ = 100 fs. (A) and (B) compare spectra with pump pulse center frequencies (arrows) of 3400 cm⁻¹ (blue-pump) and 3100 cm⁻¹ (red-pump) respectively. The spectra shown here are normalized to the absolute maximum peak intensity at the longest waiting time (6ps) in the 3600-3800 cm⁻¹ region. The frequency region below 2200 cm⁻¹ in (A) and (B) is multiplied by a factor of 4 to enhance the spectral features. The asterisk marks the region of spectral interference by atmospheric CO₂.

pump TA spectrum of 7M NaOH at 100 fs (Fig. 4-3A), a weak bleach feature in the 2350–3000 cm⁻¹ region is observed but largely overshadowed by the induced absorption from the bulk-like water molecules. In addition, there is an induced absorption in the 1350–2200 cm⁻¹ region, which is stronger and qualitatively different from neat water. A weak and broad bleach feature centered at 2000 cm⁻¹ is superimposed on top of this induced absorption along with a narrower bleach at 1680 cm⁻¹ corresponding to the H-O-H bend.
vibration of bulk-like water molecules. In contrast, the red-pump TA spectra of 7M NaOH at 100 fs shows a distinct broad bleach centered at ~2700 cm\(^{-1}\) (Fig. 4-3B), riding on top of the induced absorption from the O—H stretch of bulk-like water. The center of this spectral feature is redshifted by ~150 cm\(^{-1}\) from the hydroxide feature observed in FTIR. In TA spectra, contributions from all the frequencies in the pump pulse are inherently present. Thus, a combination of the bleach feature from the solvated OH\(^{-}\) ion at lower frequencies (2350-3000 cm\(^{-1}\)) and the induced absorption feature (peaks at 2950 cm\(^{-1}\)) from the bulk-like water molecules produces a redshift of the resultant peak when the bleach feature is stronger. The broad induced absorption at <2000 cm\(^{-1}\) is more intense in red-pump than the blue-pump TA spectrum. Due to the bend vibration of bulk-like water, the bleach, centered at 1680 cm\(^{-1}\), rides on top of this broad induced absorption, but the broad bleach centered at 2000 cm\(^{-1}\) is absent in the red-pump TA spectrum. A sharp induced absorption centered at 3640 cm\(^{-1}\) is only observed in the red-pump TA spectrum, near the vibrational frequency of the ion, and resembles a similar induced absorption observed in TA of H\(_2\)O at slightly longer waiting times (~250fs).

2DIR spectra allow us to disperse TA spectra by excitation frequency as well, revealing correlations between excitation (\(\omega_1\)) and detection frequencies (\(\omega_3\)) after a waiting time \(\tau_2\). BB 2DIR spectra of H\(_2\)O, 4M NaOH and 7M NaOH at 100 fs waiting time are shown in Fig. 4-4, where the pump pulse is centered at 3100 cm\(^{-1}\), 300 cm\(^{-1}\) redshifted from the center of the O—H stretch peak. On addition of NaOH to H\(_2\)O, a diagonal bleach peak appears at 2850 cm\(^{-1}\) (Fig. 4-4) due to the solvated OH\(^{-}\) ion. This is accompanied by a qualitatively different, intense and broad induced absorption for \(\omega_3< 2200\) cm\(^{-1}\), on which the cross peak bleach of H-O-H bend with O—H stretch of bulk-like water molecules at
Figure 4-4: BB 2DIR spectra of H₂O, 4M NaOH/H₂O and 7M NaOH/H₂O at τ₂ = 100fs, where the pump pulse center frequency is at 3100 cm⁻¹. The spectra are normalized to the absolute maximum peak intensity in the 3200-3600 cm⁻¹ region of detection frequency (ω₁). The regions below 2200 cm⁻¹ in detection frequency (ω₃) of the spectra have been multiplied by a factor of 10 to highlight the spectral features. The asterisk marks the region of spectral interference by atmospheric CO₂.

1680 cm⁻¹ is superimposed. This cross peak bleach is largely overshadowed by the strong induced absorption feature present in those frequencies. Additionally, this cross peak bleach from the bend is centered at high excitation frequency (ω₁>3300 cm⁻¹) in all samples, indicating that strong stretch-bend coupling arises in bulk-like water. The induced absorption in 4M and 7M NaOH spectrum indicates presence of a band of hydroxide-associated vibrational state, between ~4600 and 5300 cm⁻¹ above the ground state, being accessed by a second photon following O—H stretch excitation of solvated hydroxides.
Figure 4-5: Slices from the BB 2DIR spectra of H$_2$O, 4M NaOH/H$_2$O and 7M NaOH/H$_2$O at $\tau_2$ = 100 fs, taken at $\omega_1$ = 3340 cm$^{-1}$ (blue dashed lines in Fig. 4-4) and $\omega_1$ = 2908 cm$^{-1}$ (red dashed lines in Fig. 4-4) are shown in (A) and (B) respectively. The frequency region below 2200 cm$^{-1}$ in (A) and (B) is multiplied by a factor of 4 to enhance the spectral features. The asterisk marks the region of spectral interference by atmospheric CO$_2$.

To illustrate the pump frequency dependence of spectral features in the BB 2DIR spectra, we show slices from it along $\omega_3$ with fixed $\omega_1$ for blue ($\omega_1 = 3340$ cm$^{-1}$, Fig. 4-5A) and red ($\omega_1 = 2908$ cm$^{-1}$, Fig. 4-5B) excitation frequencies. The TA spectra contain the response resulting from all the frequencies within the pump pulse as opposed to a response from a single excitation frequency in the BB 2DIR slices. Thus, these slices reveal similarities along with some notable differences from the TA spectra acquired at similar pump center frequencies. Although spectral slices for two different NaOH concentrations
are shown in Fig. 4-5 in order to highlight the features resulted by OH⁻ ion, we shall refer to the spectra of highest concentration of NaOH (7M) as the differences are most distinct at higher concentrations. A comparison of the blue excitation spectra (Fig. 4-3A and 4-5A) shows that BB 2DIR spectral slices have weaker bleaches for the 1680 cm⁻¹ bend vibration of bulk-like water for both H₂O and 7M NaOH, as well as a weaker cross peak bleach at 2000 cm⁻¹ for 7M NaOH compared to TA. In the red excitation slice of the BB 2DIR spectrum of 7M NaOH, the bleach at 2850 cm⁻¹ is more pronounced than TA, and the cross peak bleach of the bend vibrations is barely visible (Fig. 4-3B and 4-5B). Comparison of blue and red slices from the BB 2DIR spectrum of 7M NaOH (Fig. 4-5A and 4-5B) highlights greatly enhanced bleaches at 2850 cm⁻¹, a stronger induced absorption <2200 cm⁻¹ and a sharp induced absorption at 3640 cm⁻¹ in the red slice. The bleach at 2000 cm⁻¹ appears only in the blue slice suggesting this feature to be related to O—H stretch transitions at higher frequencies.

Although similar features to those in Fig. 4-3, 4-4 and 4-5 are present at lower concentrations, the influence of the OH⁻ ion on the TA and BB 2DIR spectra are most apparent for concentrated solutions of aqueous hydroxides. At these high concentrations, it is a concern that ion pairing may play a role in the experimental observations. To investigate, we have analyzed concentration dependent FTIR and BB 2DIR spectra at \( \tau_2=100 \) fs using CSVD. Figure 4-6A and 4-6B show the spectral components and the corresponding concentration amplitudes of CSVD respectively, obtained from FTIR spectra in Fig. 4-1A. The first two components of CSVD almost exclusively contribute to the data (Fig. 4-6C). With the first spectral component constrained to be the FTIR spectrum of water, we find that the second spectral component (Fig. 4-6A) resembles the FTIR
Figure 4-6: (A) and (B) Singular value weighted spectral components and the corresponding concentration amplitudes of CSVD respectively, obtained from FTIR spectra in Fig. 4-1A. Blue and green lines in (B) shows linear fit to the actual data points. The second singular value weighted spectral component has been multiplied by a factor of 75 in (A) to have it on the same scale as the first component. (C) Normalized singular values of different components obtained from SVD analysis of concentration dependent FTIR (Fig. 4-1A) and BB 2DIR spectra at $\tau_2 = 100$ fs (Fig. 4-7A). Singular values of the components determine their relative contribution to the data in an SVD analysis. Majority of the contribution comes from the first 2 components in FTIR spectra and first 3 components in BB 2DIR spectra.

difference spectrum of concentrated NaOH solution and H2O (Fig. 4-1B). The contribution of the second concentration amplitude grows linearly with NaOH concentration, and the first one decreases, as expected when the concentration of water decreases with increased
hydroxide concentration (Fig. 4-6B). This behavior is expected for a two-component mixture.

Figure 4-7: (A) BB 2DIR spectra at $\tau_2 = 100$ fs of aqueous NaOH solution for five concentrations between 0 and 7M where the pump pulse is centered at 3100 cm$^{-1}$. (B) and (C) First three singular value weighted spectral components and the corresponding concentration amplitudes of CSVD respectively, obtained from BB 2DIR spectra in (A). The second and third singular value weighted spectral components have been multiplied by a factor of 50 and 150 respectively, in (B) to have them on the same scale as the first component.

A similar CSVD analysis is applied to the BB 2DIR spectra at $\tau_2=100$ fs of NaOH in H$_2$O for five concentrations between 0 and 7 M over 2425–3800 cm$^{-1}$ detection
frequencies \((\omega_3)\) (Fig. 4-7A). When the first spectral component is constrained to be the water spectrum (Fig. 4-7B), we find a slight decrease in its amplitude as the hydroxide concentration increases (Fig. 4-7C). The second spectral component, indicative of the dominant spectral changes on adding NaOH to H\(_2\)O, shows a broad diagonal bleach feature in the 2800–3200 cm\(^{-1}\) region (Fig. 4-7B). Furthermore, it appears to have a cross peak to the main O—H stretch of bulk-like water at \((\omega_1, \omega_3) = (3050, 3375)\) cm\(^{-1}\). Although the contribution of the second spectral component to the data increases monotonically with concentration, it is not linear over the entire concentration range (Fig. 4-7C). This suggests that influence of the OH\(^-\) ion on the BB 2DIR spectra is not totally captured by the second CSVD component and a combination of second and third CSVD component would be required to explain the contribution of the ion on the spectra. Here, the third spectral component of the CSVD (Fig. 4-7B) is non-negligible as it contributes \(\sim 7\%\) at the highest concentration 2D spectra (Fig. 4-6C), indicating that we cannot rule out the presence of ion pairing or collective effects involving multiple hydroxides in the high concentration 2DIR spectra. Overall, it does appear that the dominant contributor to our steady state and time-resolved infrared experiments are the water-solvated OH\(^-\) ion retaining local configurations similar to more dilute solutions.

4.3.2. Computational:

To help assign the spectral features observed in the linear and non-linear IR spectra, we compare experimental data to the HVA of H\(_2\)O and OH\(^-\) (aq.) clusters. Figure 4-8A shows the normalized DOS obtained from HVA for H\(_2\)O and OH\(^-\) (aq.) clusters using DFT. The DOS qualitatively captures the frequency shifts expected from all vibrational
transitions upon forming strong hydrogen bonds to the oxygen of the ion. Although it does capture the broadening and redshift of the O—H stretch transition, the blueshift and width of the bend vibrations do not correspond well to the experiment. The weak variation and narrow frequency distribution seems to indicate that a harmonic approximation is particularly poor for the bending modes of the ion complex. A comparison of the normalized DOS obtained from DFT and HF calculations shows the same qualitative behavior (Fig. 4-8B). Variation of peak positions and peak widths are much more prominent between DFT and HF for the bend and low frequency intermolecular vibrations compared to O—H stretch. We restrict ourselves to analysis of O—H stretch vibrations only in the subsequent part of this chapter as HVA works best for those vibrations.

**Figure 4-8:** (A) DOS of normal modes of H₂O and OH⁻ (aq.) clusters obtained using DFT, where the DOS are normalized to the area. Only the normal modes centered on core water molecules and the OH⁻ ion have been considered to better represent the bulk liquid. (B) Comparison of DFT and HF in HVA to predict the normal mode frequencies of solvated OH⁻ clusters. On an average, HF underestimates the effect of hydrogen bonding and thus calculates slightly higher frequencies for the normal modes across the spectrum. However, the differences are more pronounced in the lower frequency regions.
The resulting O—H stretch vibrations in aqueous hydroxide are delocalized. In order to determine the extent of O—H stretch delocalization in solvated hydroxide complexes, we calculate the participation ratio (PR) metric [72]. While calculating the normal modes, we first calculate the single point energy of the cluster and construct a Hessian of the potential energy. Eigenvalues of Hessian provides the harmonic frequencies of the modes and the eigenvectors, $e_i$, contain information about displacement of the atoms in $i$-th normal mode. The PR of $i$-th normal mode is defined as:

$$P_i = \left[ \frac{N}{\sum_{\alpha=1}^{3N} (e_i^\alpha \cdot e_i^\alpha)^2} \right]^{-1}$$

(4-3)

where, $N$ is the number of atoms in the cluster (53 in our case) and $\alpha$ is the total number of degrees of freedom of all the atoms (159 in our case). The PR thus defined, is on the order of $1/N$ for a local mode and on the order of 1 for a fully delocalized mode. In order to check whether the delocalization of O—H stretch vibrations are dependent on the local structure of the solvated ion, PR is calculated for 3- and 4-coordinate solvated OH$^-$ ions separately. The calculated PR for 3- and 4-coordinate complexes as a function of vibrational frequencies are presented in Fig. 4-9A and 4-9B respectively. We note that correlation between PR and vibrational frequencies of O—H stretches are poor and the distributions are almost identical for both the coordination numbers. A large fraction of vibrations have a PR between 0.025 and 0.05, which corresponds to delocalization over 4-8 water molecules. As we consider vibrations centered on core water molecules only, they are delocalized over at least the first solvation shell of a properly solvated OH$^-$ ion. This also emphasizes that the vibrations responsible for the broad continuum absorption in linear IR spectra of aqueous hydroxides cannot be treated as local modes or as independent
normal modes of the individual molecules.

![Diagram](image)

**Figure 4-9:** (A) and (B) Participation ratio of O—H stretch vibrations in 3- and 4-coordinated hydroxides respectively. Only the vibrations centered on the core water molecules are considered for this calculation.

Given the interest in determining the hydroxide coordination number and its role in proton transfer, it is natural to identify the differences in vibrational frequencies, if any, between 3 and 4-coordinated OH⁻ ions [73]. The DOS and $\rho(\omega)$ in the O—H stretch region are shown for both coordination numbers in Fig. 4-10A and 4-10B, respectively. Distribution of frequencies for both coordination numbers are very broad and overlapping. The primary distinction between them is the O—H stretch vibration peaks ~150 cm⁻¹ higher in frequency for 4-coordinate species compared to 3-coordinate ones, which is small compared to ~700 cm⁻¹ width of their distribution. Though, average hydrogen bond distances are 7.5% lower on in 3-coordinate species compared to 4-coordinate species, their distribution varies considerably within a particular cluster as well as between clusters of...
same coordination number. Such a large variation in the solvation structure within 3- and 4-coordinate configurations results vibrational frequencies so overlapped that one cannot effectively distinguish them in solution spectra. Thus, the count of hydrogen bonds is not a good predictor for the vibrational frequency, as much as the strength of interaction of specific waters with the ion.

Figure 4-10: (A) DOS and (B) \( \rho(\omega) \) for coupled O—H stretch vibrations of the core water molecules and the \( \text{OH}^- \) ion for 3-coordinate and 4-coordinate species obtained using DFT. Both the DOS and \( \rho(\omega) \) are normalized to the peak maximum. Contributions of vibrations centered on the \( \text{OH}^- \) ion towards \( \rho(\omega) \) have been multiplied by a factor of 50 in (B) to bring them on the same scale.

Additionally, we have determined the contribution to the DOS and \( \rho(\omega) \) from the
vibrations of the O—H bond of the OH\(^-\) ion itself (Fig. 4-10A and 4-10B). Similar to the collective O—H stretch vibrations of first solvation shell water molecules, O—H stretch vibration of the ion itself is indistinguishable between 3- and 4-coordinate solvated hydroxides. Since the proton of the ion interacts weakly with its surroundings, this vibration is distinctly localized on the ion and of a significantly higher frequency, peaking near 3700 cm\(^{-1}\). Furthermore, its weak transition dipole moment leads to a relatively small contribution to the spectral density, explaining the ion’s negligibly small contribution to the FTIR spectrum. The width of the distribution of ion frequencies (325–400 cm\(^{-1}\)) is large compared to the linewidth observed in Raman spectra (50 cm\(^{-1}\)) [64–66]. Previous works on the calculation of O—H stretch frequencies of OH\(^-\) ion in aqueous solutions have shown that without inclusion of motional narrowing effects, one can have a broad distribution of calculated frequencies [66].

Moreover, there is no clear correlation between the normal mode frequencies of O—H stretch vibrations and the distribution of hydrogen bond distances or average hydrogen bond distances of the solvating waters of a particular cluster, as shown in Fig. 4-11. This leads us to conclude that the structural parameters, in general, are poor predictors of vibrational frequencies for these systems. Since collective metrics, such as the solvent electric field [74–77] and solvation energy [78], correlate well to local mode O—H stretch vibrations in isotopically diluted water and hydroxides along with playing an important role in proton movement, such metrics may play a more important role in determining the vibrational frequency of the collective modes of solvated hydroxides as well along with dictating proton transport process.
Figure 4-11: (A) and (C) shows correlation between normal mode frequencies of O—H stretch and mean values of $R_{OH}$ in different clusters of 3- and 4-coordinate solvated $OH^-$ ions respectively. (B) and (D) shows correlation between normal mode frequencies of O—H stretch and range of values of $R_{OH}$ in different clusters of 3- and 4-coordinate solvated $OH^-$ ions respectively.

Since the calculated O—H stretch normal modes involve the collective vibration of waters solvating the ion, symmetry should play a key role in the spectroscopy of the complex. Thus, we have classified the normal modes of the complex into symmetric and asymmetric vibrations based on the relative phases of vibrations of the O—H bonds of first solvation shell water molecules hydrogen bonded to the ion, as illustrated in Fig. 4-12. The designations are based on the $C_{3v}$ or $C_{4v}$ symmetry for ideal 3- and 4-coordinated solvated hydroxide ions, although the solvated hydroxide ion never experiences ideal symmetry for
Figure 4-12: Coupled O—H stretch vibrations of first solvation shell H₂O molecules in 3-coordinate and 4-coordinate OH⁻ ions. Symmetries of each of the vibrations are assigned based on the relative phases of vibration of the O—H bonds solvating the OH⁻ ion. The symmetry designations are based on perfect C₃ᵥ or C₄ᵥ molecules corresponding to 3- and 4-coordinated OH⁻ ions respectively. The asymmetric X vibration for 4-coordinate species can be reduced to E-E'+A₁+A₂.
the calculated clusters. For a typical 3-coordinate species, there are two different types of vibrations: (1) the $A$ mode, a symmetric vibration with all O—H bonds of the solvation shell waters hydrogen bonded to the ion vibrating in-phase, and (2) the asymmetric $E$ mode where one of the O—H bonds vibrate out of phase to the other two (Fig. 4-12). For 4-coordinate species, we have one symmetric $A_1$ mode and asymmetric vibrations of $E$ and $A_2$ character as shown in Fig. 4-12. We also find modes with one O—H bond in the first solvation shell vibrating in opposite phase to the other three. Since this is not an irreducible representation, we designate this as $X$, an asymmetric vibration.

![Graph](image)

**Figure 4-13:** (A) $\rho(\omega)$ of symmetric and asymmetric stretch vibrations of 3- and 4-coordinate OH$^-$ ions obtained using DFT where $\rho(\omega)$ for both symmetries have been normalized to the peak of asymmetric vibrations of the corresponding coordination number. (B) Comparison of $\rho(\omega)$ for three different types of asymmetric O—H stretch vibrations in 4-coordinate solvated OH$^-$ ion.
The resulting symmetry decomposition of $\rho(\omega)$ for the O—H stretch vibrations is shown in Fig. 4-13A. The asymmetric stretch vibrations are $\sim 800$ cm$^{-1}$ broad compared to the $\sim 600$ cm$^{-1}$ width of symmetric vibrations regardless of coordination number. For both 3- and 4-coordinate species, the asymmetric stretch vibrations peak $\sim 500$ cm$^{-1}$ lower in frequency compared to the symmetric stretch vibrations and the intensities of asymmetric vibrations are at least a factor of two more than that of the symmetric vibrations. However, the different asymmetric vibrations in 4-coordinate species are indistinguishable by their O—H stretch frequencies (Fig. 4-13B).

4.4. Discussion:

Though the continuum absorption in the linear spectra of aqueous NaOH has limited features, the distinct nature of peaks seen in FTIR and BB 2DIR spectra and their correspondence with HVA allows us to assign some of it based on the symmetry of O—H stretch vibrations of the first solvation shell water molecules. It can be seen from HVA that the asymmetric stretch vibrations are stronger and redshifted from the symmetric stretch vibrations regardless of solvation structure of the ion (Fig. 4-13A). On this basis, we assign the shoulder in the FTIR spectra of aqueous NaOH solutions at 2850 cm$^{-1}$ (Fig. 4-1A) to asymmetric stretch vibrations of the aqueous hydroxide complex, without specifying 3- or 4-coordinate species.

HVA calculations predict that the symmetric stretch is blueshifted by $\sim 500$ cm$^{-1}$ from the asymmetric stretch. Previous calculations of O—D stretch vibration in 15M KOD solution has shown two distinct peaks separated by 350 cm$^{-1}$ and the redshifted peak between the two to be more intense [14]. Though there has not been much interpretation of
those spectral features, we believe they involved asymmetric and symmetric O—D stretches. In case of O—H stretch vibrations, although we do not take the outcomes of HVA quantitatively, it is reasonable to expect the peak of the symmetric stretch vibrations to be blueshifted by 400-550 cm$^{-1}$ given that O—H stretch vibration is broader in H$_2$O compared to O—D stretch vibration in D$_2$O. Thus, the symmetric stretch vibration should appear in the frequency window of 3250-3400 cm$^{-1}$, which is coincident with the O—H stretch vibration of bulk-like water molecules.

For a large (~500 cm$^{-1}$) splitting to occur between the asymmetric and symmetric stretch vibrations, couplings between local O—H stretches of the hydroxide complex must be very large. We have carried out a simple model calculation to estimate the coupling between local O—H stretches. A Hamiltonian is constructed with diagonal entries as degenerate site frequencies for the O—H stretches (3200-3500 cm$^{-1}$) and we have considered coupling between nearest neighbors only as off-diagonal elements. Diagonalization of the Hamiltonian provides us with the energies one would expect for normal modes. We find that, in order to have the observed splitting between different vibrations, the coupling has to be ~150 cm$^{-1}$, considerably stronger than the expected transition dipole coupling of ~50 cm$^{-1}$ [79]. A positive sign of all these couplings, also expected in case of transition dipole coupling, is required for having asymmetric stretches at lower frequencies than symmetric stretches. At the same time, resultant dipole moments for symmetric stretch vibrations are smaller compared to asymmetric stretches due to the geometry of the solvated ions. As a result, intensities for asymmetric stretch vibrations are larger compared to symmetric stretches, consistent with our observations.

Coupling between these asymmetric stretches and the symmetric stretches/O—H
stretches of bulk-like water are observed as cross peaks in the BB 2DIR spectra, which become evident in the second CSVD component spectrum (Fig. 4-7B). One way of getting information about the relative orientation of the transition dipoles of asymmetric and symmetric stretch vibrations is to measure the difference in intensity of the cross peaks with respect to the diagonal peaks in polarization dependent BB 2DIR experiments.

![BB 2DIR spectra of 7M NaOH in H2O at τ2 = 100fs at parallel (ZZZZ) and perpendicular (ZZYY) polarization geometry.](image)

**Figure 4-14:** BB 2DIR spectra of 7M NaOH in H2O at τ2 = 100fs at parallel (ZZZZ) and perpendicular (ZZYY) polarization geometry, where the pump pulse is centered at 3100 cm⁻¹. The spectra are normalized to the absolute maximum peak intensity in the 3200-3600 cm⁻¹ region of detection frequency (ω₁). There is no significant difference in the cross peak intensities with respect to the diagonal peak intensities across the polarization geometries.

However, changing polarization geometry of the BB 2DIR experiment has a minor effect on the cross peak between asymmetric stretch and symmetric stretch/O—H stretch of bulk-like water molecules in 7M NaOH solution (Fig. 4-14). In the normal modes
illustrated in Fig. 4-12, the relative displacements of the atoms have a broad distribution even within a particular symmetry of vibration. Consequently, the orientations of the transition dipoles for all symmetries have a broad distribution. On top of that, spectrally overlapping asymmetric stretch vibrations of 4-coordinate species have different orientations for the transition dipole. These explains minor effect of polarization of the incident fields on the cross peak between different symmetries.

Analysis of bend vibrations using HVA predicts that the H-O-H bend vibrations of water molecules solvating the OH⁻ ion are blue shifted on average by 100 cm⁻¹ from neat H₂O. Since bulk-like water bends are observed at 1650 cm⁻¹, the 2000 cm⁻¹ feature in FTIR of hydroxide solutions (Fig. 4-1) cannot be conclusively assigned as a bend. It seems unreasonable to assign the 2850 and 2000 cm⁻¹ peaks to symmetric and asymmetric stretches respectively, based on the frequency and intensity discrepancies with the HVA. Nor is it reasonable to assume that the frequency of the bend in the strongly hydrogen bonded OH⁻ complex is unchanged from neat H₂O. Given the absence of additional vibrations near 2000 cm⁻¹ in HVA and the shortcomings of a harmonic treatment of these vibrations, we believe that a highly anharmonic mixed intermolecular vibration with substantial bend and librational character is responsible for the 2000 cm⁻¹ peak. In case of pure H₂O, librations were found to contribute significantly to the transient absorption signal in the 800-1700 cm⁻¹ range [49]. In aqueous hydroxides, the librations are expected to blueshift due to stronger hydrogen bonds and hence can contribute to the 2000 cm⁻¹ feature. The contribution of bend vibration in this feature is supported by the fact that cross peak bleach at 2000 cm⁻¹ is observed in TA and BB 2DIR spectra only with higher frequency O—H stretches, where the symmetric O—H stretch vibrations absorb. Based on symmetry
criteria, symmetric stretch vibrations are likely to couple with bend vibrations. Unusual combination bands remain a possibility for the 2000 cm\(^{-1}\) peak, given its proximity to the bend+libration combination band of pure H\(_2\)O at 2150 cm\(^{-1}\), but higher level anharmonic calculations are required to test for such possibilities.

In neat water and aqueous hydroxides, the stretch, bend and intermolecular vibrations including librations and hydrogen bond vibrations are strongly coupled to each other, as discussed in detail in the later part of the section and in chapter 5. Upon excitation of O—H stretch vibrations, we observe cross peak bleach of bend vibrations and signatures similar to thermal difference spectra in TA and BB 2DIR spectra at very early waiting times (100–300 fs) in both neat water and aqueous hydroxides. This indicates almost instantaneous excitation of bend and intermolecular vibrations as a result exciting the O—H stretches. Nevertheless, O—H stretch remains the dominant contributor to higher frequency vibrations in the 2800–3600 cm\(^{-1}\) region. Thus, HVA adds significantly to the qualitative understanding of the spectral features in aqueous hydroxides even though it does predict the normal mode vibrations to have predominantly one of stretch, bend or intermolecular characters.

It is also worth pointing out that the results of HVA may quantitatively vary based on the detail of MD simulation from which the snapshots are taken. The changes can occur in the form of absolute position of the peaks and/or their widths. As the outcome of this analysis are consequences of large variation of solvation environment across independently chosen snapshots resulted by the fluctuation in the hydrogen bonding network in water, the qualitative features of HVA should largely remain the same.

HVA on solvated hydroxide clusters shows that O—H stretch vibrations are
delocalized over 4–8 water molecules on average, although static vibrational frequency calculations on a rapidly evolving system such as the one studied here will tend to overestimate the delocalization. Within the framework of HVA, the frequencies of these vibrations are not well correlated with geometric parameters of the solvated ions, like coordination number or hydrogen bond distances. This stands in contrast to spectroscopy of gas-phase OH\(^-\) clusters in which the local configurations are well-defined, and the 3- and 4-coordinate species are readily separated by frequency largely due to absence of a second solvation shell [21]. HVA shows that due to large variation in the solvation structure within 3- and 4-coordinate configurations, O—H stretch frequencies of both these species are almost identical. It also raises the question of whether coordination number is a useful quantity for characterizing hydroxide dynamics in liquid water. For vibrational spectroscopy, the observed structure will be averaged over a “shutter speed” given by vibrational dephasing, probably ~100 fs, which is a long enough time period that librational motions can act to switch the “instantaneous” coordination number.

Even though we primarily focused on the vibrational signatures of water solvated OH\(^-\) ions, there are some spectral features in the TA and BB 2DIR spectra, common to both neat water and aqueous hydroxides. Such features, common to strongly hydrogen bonded systems, are interpreted in light of recent evidence that the intra- and intermolecular vibrations are mixed into delocalized states in the neat liquid [47–50]. Upon excitation of O—H stretch vibrations in H\(_2\)O, the appearance of a bend cross peak and signatures similar to thermal difference spectra in TA and BB 2DIR spectra at early waiting times (Figs. 4-3, 4-4, 4-5 and 4-8) indicate strong mixing of bend and intermolecular vibrations with the O—H stretches. Further, the cross peak bleach is blueshifted by 30 cm\(^{-1}\) from the linear
absorption peak of bend vibration, indicating the presence of a Fermi resonance between the fundamental of O—H stretch and overtone of H-O-H bend vibration [47,67]. Due to the large anharmonicity, coupling of O—H stretch vibrations with bend and intermolecular modes is much more effective moving higher up in the exciton manifold, resulting in a significantly low energy gap between one- and two-exciton states. Thus, the broad induced absorption in TA and BB 2DIR spectra of H$_2$O, which stretches from 3100 to $<1350$ cm$^{-1}$, originate from absorption of two sequential mid-IR photons with energies in the range of 3200–3600 cm$^{-1}$ and 1000–3000 cm$^{-1}$ respectively. As one-photon absorption is spectrally clear in the corresponding ~4000–6500 cm$^{-1}$ region, [80] this band is a doubly excited two-exciton state which has a weak cross-section for direct absorption. These observations, combined with the finding of vibrational relaxation processes at all frequencies occur with fast time-scales compared to structural evolution of the liquid, point toward a picture of vibrations in H$_2$O that are delocalized, rapidly evolving, and of mixed inter- and intramolecular character [47–50].

When an OH$^-$ ion is embedded in a medium with these vibrations, it seems likely that the strong hydrogen bonding to the ion would somewhat localize but not eliminate the collective nature of the vibrations of the complex. A local description of the ion and first solvation shell appears to be a good starting point. Even so, it is apparent that a discussion of the vibrations and spectroscopy of the aqueous hydroxide complex using the language of normal modes is unsatisfactory. Anharmonic interactions involving multiple degrees of freedom and vibrationally non-adiabatic processes must be accounted for. In light of these findings, and recent reports that non-adiabatic dynamics are crucial to understanding the spectroscopy of ice and water [79-81], new ways of describing the vibrations of water are
needed. A model comprising of strongly coupled stretch, bend and intermolecular vibrations is used in chapter 5 to describe the spectroscopy of these systems.

The red slice of BB 2DIR spectra and the red-pump TA spectra of 7M NaOH spectra show a sharp induced absorption at 3640 cm⁻¹ (Fig. 4-3B and 4-5B) which is observed as a cross peak at \((\omega_1, \omega_3) = (3050, 3640)\) cm⁻¹ in the second CSVD component spectrum (Fig. 4-7B). While this induced absorption could result from coupling between asymmetric stretches and O—H stretch vibration of the OH⁻ ion, absence of a corresponding bleach feature in the cross peak renders this possibility unlikely. However, this peak is nearly identical to an induced absorption observed in TA and BB 2DIR experiments of H₂O at a slightly longer waiting time. Further, this feature is indistinguishable from a peak observed in thermal difference spectra (\(\Delta T = 2-3^\circ C\)) of aqueous hydroxide solutions. Previous works on pumping bend vibration and probing stretch vibration in liquid H₂O observed this type of an induced absorption at early waiting times, attributing it to stretch-bend coupling in H₂O [50]. The observation that spectral relaxation on timescales faster than solvent reorganization leads to features that mimic equilibrium temperature rises is a further indication that the eigenstates of H₂O and OH⁻ complex vibrations have strong coupling to bend and intermolecular vibrations [47,49,50].

In order to summarize our conclusions based on the experimental results and modeling described in the previous section, we present an energy level diagram, shown in Fig. 4-15, which contains the bands expected in liquid water and the additional bands available to an aqueous OH⁻ ion. Transitions for neat H₂O show pump-excitation into a band of delocalized stretch vibrations with some bend and intermolecular character, whereas in hydroxide, one also has the possibility of exciting collective symmetric and
asymmetric vibrations of the complex. While distinct resonances are present at one-quantum of excitation, two-quantum excitation in H₂O and OH⁻(aq.) involves transitions into overtone and combination bands that appear as, or are superimposed on a continuum. In H₂O, we have argued that a band of low lying vibrational two-exciton states exist that represent significant mixing of bend and intermolecular modes into stretch vibrations and has a weak cross-section for direct absorption. This comes from a comparison of the induced absorption in nonlinear spectra with the absence of comparable

**Figure 4-15:** The energy level diagram showing the fundamentals, overtones and combination bands for pure H₂O and aqueous hydroxide. The vibrational two-exciton (2-Ex) states for both H₂O and aqueous hydroxide have highly mixed intra- and intermolecular character. The double headed arrows in the figure indicate bleach transitions and single headed arrows indicate induced absorption transitions observed in the nonlinear spectra. (Right panel) Near and mid-IR spectra of H₂O (blue trace) and 7M NaOH/H₂O (green trace) are plotted vertically for comparison.
features linear near-IR spectra (Fig. 4-15, right panel). In aqueous hydroxides, the 4000–7500 cm\(^{-1}\) region in linear and nonlinear spectra appears to contain a continuum of transitions to mixed modes involving combinations of stretches, bends and intermolecular vibrations due to vibrations of the OH\(^{-}\) complex and the surrounding water. We also designate this as a two-exciton band that exists between 4000–7000 cm\(^{-1}\). Although the character of the vibrations within this band may have more stretch character higher in the band and more bend character lower in the band, as well as varying degrees of intermolecular motion, overall there is little to distinguish clear modes of vibration for excitations. The only exception appears to be the vibration of the OH\(^{-}\) ion itself, which shows a clear overtone in the near IR spectrum.

### 4.5. Conclusions:

We have used TA and BB 2DIR experiments in conjunction with HVA to provide an assignment of the different spectral features observed in infrared spectroscopy of aqueous hydroxides. The O—H stretch vibrations in aqueous hydroxides are delocalized in nature and geometric structural parameters do not correlate well with the frequencies. The 3- and 4-coordinate species of solvated OH\(^{-}\) ions in aqueous media are not distinguished based on their infrared spectroscopic signatures, largely due to inhomogeneity in the environment of the solvated ion. However, O—H stretch vibrations of the solvated ions can be classified based on symmetry, defined by the relative phase of vibrations of the individual O—H bonds hydrogen bonded to the ion. The asymmetric stretch vibrations are found to have lower frequencies than the symmetric ones and are at least twice as intense. Based on this observation, we assign the shoulder centered at 2850
cm\(^{-1}\) in the FTIR spectra and the diagonal peak at the same frequency in the BB 2DIR spectra of aqueous NaOH to asymmetric stretch vibrations. On the other hand, symmetric stretch vibrations, absorbing in the 3250-3400 cm\(^{-1}\) region, is overshadowed by the O—H stretch of bulk-like water molecules. Though inconclusive from HVA, based on our experimental results, we believe that the broad and weak absorption feature at 2000 cm\(^{-1}\) in the ATR FTIR difference spectrum and nonlinear IR spectra of aqueous NaOH, involves coupled bend vibrations of solvating water molecules.

Alongside these features for solvated hydroxide ions, we observe signatures of strong coupling between intra- and intermolecular vibrations in both neat water and aqueous hydroxides. The spectral assignments along with a consideration of coupled intra- and intermolecular vibrations, provide the ground work to understand time-dependent relaxation processes and the dynamics of proton transport in hydroxide solutions using ultrafast nonlinear IR spectroscopies.

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References:


4.A. Appendix: Pump frequency dependent BB 2DIR spectra of H₂O and 7M NaOH

Pump center frequency dependent BB 2DIR spectra of H₂O and 7M NaOH shows a few interesting features. The spectra look more inhomogeneous when the pump center frequency is tuned to higher frequencies, closer to the peak of O—H stretch vibration. The BB 2DIR spectra are essentially convolution of the third order nonlinear response function with the pump and probe spectra. That is why the center of the bleach feature follows the center of the pump frequency and starts to look homogeneous when the pump center is detuned from the peak of O—H stretch vibration.

In 7M NaOH spectra, the cross peak bleach at 2000 cm⁻¹ creates two artificial peaks on the induced absorption feature, when the pump center frequency is tuned blue. On the other hand, the diagonal bleach feature at 2850 cm⁻¹ distinctively appears only when the pump pulse is centered red.
Figure 4-A1: BB 2DIR spectra of H₂O and 7M NaOH/H₂O at τ₂ = 100fs, where the pump pulse center frequency is varied (blue: 3400 cm⁻¹, cyan: 3270 cm⁻¹, green: 3200 cm⁻¹ and red: 3100 cm⁻¹). The pump spectra are shown on top of the corresponding BB 2DIR spectra. The spectra are normalized to the absolute maximum peak intensity in the 3200-3600 cm⁻¹ region of detection frequency (ω₁). The regions below 2200 cm⁻¹ in detection frequency (ω₃) of the spectra have been multiplied by a factor to highlight the spectral features. The asterisk marks the region of spectral interference by atmospheric CO₂.
Chapter 5

Vibrational Dynamics of Aqueous Hydroxide Solutions Probed using Broadband 2DIR Spectroscopy

5.1. Introduction:

Proton transport (PT) in aqueous hydroxide solutions is anomalously fast due to the aid of water’s hydrogen bonds in movement of a proton from a solvating water molecule to the OH⁻ ion [1,2]. Even though there is lack of consensus regarding the mechanism of PT, numerous theoretical and experimental works conducted over the last few decades appreciate the role of dynamic hydrogen bonding network of water molecules for successful PT to varying degree [3–16]. Fluctuations in the hydrogen bonding network of water takes place on femtoseconds to picoseconds timescale. Therefore, an understanding of the dynamics of hydrogen bonding network of solvating water molecules is critical in formulating a description of PT in aqueous hydroxide solution.

Few different mechanisms for PT in aqueous hydroxide has emerged based on different molecular dynamics (MD) simulations, occasionally with some experimental evidences [3,5,10,12–16]. Majority of these suggestions describe proton transport in terms of interconversion between stable solvated structures of hydroxide ions. One of the
proposition argues in favor of a 3-coordinate stable solvated structure of hydroxide ions (H\textsubscript{3}O\textsubscript{4}\textsuperscript{-}), analogous to Eigen cation in aqueous acid solution. In this picture, PT takes place via a stable H\textsubscript{3}O\textsubscript{2}\textsuperscript{-} intermediate, similar to Zundel cation in aqueous acids [3,6,17,18]. Recent developments of ab-initio MD (AIMD) and empirical valence bond MD (EVB-MD) simulations have called this mechanism into question. These results point toward a 4-coordinate stable structure of the hydroxide ions in aqueous solution, where the ion accepts four hydrogen bonds [4,5,7,8,11,12,19–23]. During PT, it is proposed to lose one solvating water molecule to get into a 3-coordinate structure that can be viewed as a solvated H\textsubscript{3}O\textsubscript{2}\textsuperscript{-} species. Subsequently, the proton shuttles between two water molecules on ~180 fs timescale before being successfully transferred on few picoseconds timescale [7,8,12]. Both these descriptions take into account changes in local structure of the hydroxide ions but understates the collective effect of hydrogen bond fluctuation of solvating water molecules beyond first solvation shell of the ions. Ultrafast nonlinear infrared (IR) spectroscopy on isotope diluted aqueous hydroxide solutions provide evidences in favor of fleeting existence (~110-120 fs) of the Zundel-like species of during PT [10,13,24]. On the other hand, a successful PT is found to take place on ~3 ps timescale [13]. However, these experimental results point toward a picture of PT that requires consideration beyond changes in local structure of the ion.

More recently, some AIMD studies point towards a multiscale and multidynamical picture of PT, where changes in the hydrogen bonding network of solvating waters is proposed to be the guiding factor [15,25]. A proton is proposed to have long range transport across 2-3 water molecules due to contraction of hydrogen bonding network of water, after attaining a favorable configuration. In this picture, the rate of PT is essentially determined
by attainment of such favorable configurations which could take a few picoseconds to occur. Analysis of EVB-MD simulations indicate collective electric fields of solvating water molecules along the proton transfer direction to be a the reaction coordinate in such scenarios, rather than changes in local structure of the solvated hydroxide ion [16]. Even though a proton can shuttle between two water molecules on few hundreds of fs timescale, collective rearrangement of the hydrogen bonding network of water molecules favoring transport of proton and subsequent solvation of newly formed hydroxide ions takes few picoseconds to occur, much like transport of protons in aqueous acid solutions [26–28].

Much of the understanding on PT in aqueous hydroxides is obtained from MD simulations and direct experimental evidence in favor of them is limited. Ultrafast nonlinear IR spectroscopy is a suited candidate to study this problem due to its ability to monitor exchange between different vibrations and their relaxation with time resolution of few tens of femtoseconds. Hydrogen bonds formed by the hydroxide ion with solvating water molecules are stronger compared to that in neat water. It results a broad continuum absorption in the 1000-4000 cm\(^{-1}\) region with limited spectral features. Such a feature, centered at 2850 cm\(^{-1}\), has been assigned to asymmetric O—H stretch vibrations of the water molecules solvating the OH\(^{-}\) ions (Fig. 5-1), as described in detail in chapter 4. A <70 fs broadband infrared (BBIR) source spanning from <400 cm\(^{-1}\) to 4000 cm\(^{-1}\) enables us to probe the entire mid-IR continuum absorption of aqueous hydroxides. We employ ultrafast IR transient absorption (TA) and broadband 2DIR (BB 2DIR) experiments on aqueous NaOH solution where we excite the O—H stretch vibrations of aqueous hydroxide solutions, and probe the response between 1600 and 3800 cm\(^{-1}\). These experiments investigate exchange between vibrations due to solvated hydroxide ion and bulk-like water
molecules alongside monitoring their vibrational relaxation behavior.

![FTIR spectra of H₂O and aqueous NaOH solutions](image)

**Figure 5-1:** FTIR spectra of H₂O and aqueous NaOH solutions of concentrations ranging from 3M to 10M. The spectra are normalized to the maximum of O—H stretch peak at 3400 cm⁻¹. The blue and red shaded regions correspond to O—H stretch vibrations of bulk-like water molecules and asymmetric stretch vibrations of water molecules solvating the hydroxide ion, respectively.

It is worth mentioning that vibrations in isotopically pure liquid water and aqueous hydroxides are delocalized in nature [29–35]. BB 2DIR experiments in conjunction with harmonic vibration analysis and orientational relaxation measurements in aqueous NaOH indicate that vibrations associated with solvated hydroxide to be delocalized over 4-8 water molecules [35]. A dynamical study of these vibrations could potentially inform about the importance of solvating water molecules in second and subsequent solvation shells of the OH⁻ ion in PT.
5.2. Experimental Methods:

The experimental procedure for performing TA and BB 2DIR spectroscopy is discussed in detail in chapter 3, therefore, only a brief description is given here. Mid-IR pulses for these experiments are generated by two separate sources, each of which uses 1 kHz repetition rate sub-25 fs 800 nm pulses out of a Ti:sapphire regenerative amplifier as input. We use sub-45 fs transform-limited pulses centered around 3 μm to pump different O—H stretching vibrations. These pulses are generated by a KNbO3 optical parametric amplifier (OPA) [36]. The OPA has a bandwidth of ~400 cm⁻¹ and its center frequency can be tuned between 3100 and 3500 cm⁻¹. As probe pulses in the TA and BB 2DIR experiments, we use a <70 fs BBIR pulse that probes the entire continuum region including the O—H stretches [37]. Time-coincident fundamental, second, and third harmonic of the 800 nm pulses out of the Ti:sapphire amplifier are focused in dry air to generate a plasma that radiates BBIR pulses with frequencies ranging from <400 to 4000 cm⁻¹. The BBIR beam is separated from the visible by passing through a 400 μm thick high-resistivity Si wafer placed at Brewster’s angle and is collimated at ~15 mm. The BBIR pulse is temporally characterized by cross-correlation with a sub-45 fs 3 μm pulse which gives an instrument response time of ~70 fs.

BB 2DIR experiments reported in this chapter are performed in the pump-probe geometry [38], where the first two interactions of the sample are with a collinearly propagating 3 μm pulse pair and the BBIR pulse acts as a probe. The 3 μm pulse pair is generated from the OPA output using a Mach-Zehnder interferometer. The fixed arm of the interferometer is mechanically chopped at half the laser repetition rate and the other arm is sent to an interferometrically calibrated translation stage. The time delay between
the 3 μm pulses (τ₁) is numerically Fourier transformed to obtain the excitation frequency axis ω₁. While performing the TA experiments, the moving arm of the 3 μm interferometer is blocked. Waiting time (τ₂) between the pump and the probe pulses for these experiments is set by a separate delay stage that introduces a time delay into the 800 nm input pulse used for BBIR generation. The BB 2DIR experiments reported in this chapter are performed in parallel polarization (ZZZZ) geometry. On the other hand, the TA experiments use magic angle (angle between pump and probe pulse is 54.7°) polarization geometry for measuring vibrational relaxation timescale. In order to measure rotational anisotropy, the TA experiments and performed in both parallel and perpendicular geometry with same pump power. Thereafter, the anisotropy signal, r(t) is obtained by:

\[
    r(t) = \frac{S_{∥} - S_{⊥}}{S_{∥} + 2S_{⊥}}
\]  

(5-1)

Where, \( S_{∥} \) and \( S_{⊥} \) are TA signals at parallel and perpendicular geometries respectively. However, due to large noise in the anisotropy spectra, we often plot the difference spectra between parallel and perpendicular polarization geometry.

To detect the BBIR pulse, we disperse it on a 64-element HgCdTe (MCT) array detector with a lower frequency cutoff of 1350 cm⁻¹. The signal of TA and BB 2DIR experiments is acquired for each detector element as a change in absorbance, \( \Delta A = -\log(I/I_0) \) where \( I \) and \( I_0 \) are the intensities of the probe pulse with and without the pump pulse(s), respectively. Due to the large bandwidth of BBIR pulses and limited number of array pixels, we have used three grating positions to collect the entire BBIR spectrum with an overlap of at least 65 cm⁻¹ between two consecutive grating positions.
Finally, a complete spectra is obtained by taking an average of the signal in the spectral overlap region between two consecutive grating positions during post-processing of the data. Higher order diffraction effects from the 3000-3500 cm$^{-1}$ region of the spectra produce artifacts to the measured signal in the 1500-1750 cm$^{-1}$ and 1000-1170 cm$^{-1}$ region. We place a 2200 cm$^{-1}$ long pass filter in front of the detector while collecting data in the 1350–2055 cm$^{-1}$ region in order to avoid such artifacts.

The TA and BB 2DIR spectra presented in this chapter have been normalized to the absolute maximum peak intensity in the 3600–3800 cm$^{-1}$ region at the longest waiting time (6 ps) and in the 3200–3600 cm$^{-1}$ region of detection frequency ($\omega_3$), respectively. While collecting the BB 2DIR spectra of aqueous NaOH, the pump pulses vary slightly across different concentrations. Division by the pump spectra along $\omega_1$ to obtain a normalized spectra does not work as the width of peaks are about the same or larger compared to the width of the pump spectrum. In order to have uniformity, the BB 2DIR spectra are first divided along the $\omega_1$ axis by the pump spectrum for which the data is acquired, and then multiplied by the pump spectrum used to acquire the highest concentration of NaOH (7M) at 100 fs waiting time.

The TA and BB 2DIR experiments are performed in transmission mode. The sample is sandwiched without a spacer between two 1 mm thick CaF$_2$ windows (pathlength ~2 μm) leading to an absorbance of 0.8–1.0 for the peak of the O—H stretch vibration in H$_2$O as well as in aqueous NaOH solutions of concentrations up to 10M. Aqueous solutions of NaOH are prepared by dissolving NaOH pellets (Mallinckrodt, ≥98% assay) in H$_2$O (purified by reverse osmosis to a resistance of 18 MΩ).
5.3. Results and Discussion:

In order to study time dependent changes of vibrational features corresponding to solvated OH⁻ ions, we have collected waiting time dependent BB 2DIR spectra of aqueous NaOH. Figure 5-2 compares waiting time dependent BB 2DIR spectra of neat H₂O and aqueous NaOH in order to identify the vibrational signatures due to the solvated OH⁻ ion from that of water. At early waiting times (τ₂=100 fs), BB 2DIR spectra of neat water show a diagonal bleach of O—H stretch vibration in the 3000-3400 cm⁻¹ region, a corresponding broad induced absorption that peaks at 2950 cm⁻¹ but is extended past 1500 cm⁻¹; and a cross peak bleach of H-O-H bend vibration at 1680 cm⁻¹. In the case of 7M NaOH solution, we observe an additional diagonal bleach peak at 2850 cm⁻¹ corresponding to asymmetric O—H stretch vibration of water molecules solvating the OH⁻ ion. The diagonal bleach corresponding to symmetric O—H stretch vibrations are overlapped with the O—H stretch vibrations of bulk-like water molecules. At the same time, qualitatively different induced absorption feature in 7M NaOH below 2200 cm⁻¹ arises from transitions to combination bands and overtones of hydroxide associated states.

The decay of the induced absorption features in both neat H₂O and 7M NaOH signifies vibrational relaxation, which occurs on 150-300 fs timescale, as discussed in detail later in this section. At longer waiting times (≥1 ps), the BB 2DIR spectra resembles “thermal difference” (ΔT=2-3⁰) spectra for both the systems. With increase in temperature, the hydrogen bonds in neat H₂O and 7M NaOH become weaker, resulting in a blueshift of the O—H stretch vibrations and redshift of the H-O-H bend vibrations. Therefore, a “thermal difference” spectra with positive temperature difference show induced absorption features at higher and lower frequencies compared to corresponding bleaches in the O—H
Figure 5-2: BB 2DIR spectra of H$_2$O (top row) and 7M NaOH (bottom row) as a function of waiting time, $\tau_2$. The pump pulse is centered at 3100 cm$^{-1}$ while acquiring these spectra. The spectra are normalized to the absolute maximum peak intensity in the 3200-3600 cm$^{-1}$ region of detection frequency ($\omega_3$). The region below 2200 cm$^{-1}$ in $\omega_3$ is multiplied by a factor of 15 to highlight the spectral features. The asterisks mark the region of spectral interference by atmospheric CO$_2$. 

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stretch and H-O-H bend regions, respectively. However, signatures of “thermal difference” spectra is observed as early as 200 fs in neat water and at 100 fs in 7M NaOH. Structural rearrangement of the liquid takes place on a timescale of 1-2 ps, which is even slower in concentrated hydroxide solutions due to the presence of stronger hydrogen bonds, reflected in their higher viscosity [13]. Therefore, such spectral features appearing at early waiting times cannot be a result of thermal difference due to relaxation of the vibrations. In order to explain such observations, we need to take into account strong anharmonic coupling between intra- and intermolecular vibrations, as shown in detail in chapter 6.

The pump pulses in these experiments are centered at 3100 cm\(^{-1}\), 300 cm\(^{-1}\) below the peak of O—H stretch vibration of bulk/bulk-like water. The experimental BB 2DIR spectra are essentially convolution of third-order nonlinear response with the pump spectra. As a result of the off-centered pump pulses, the diagonal bleach feature in the 3000-3400 cm\(^{-1}\) region looks homogeneous for both neat H\(_2\)O and 7M NaOH solution, even at early waiting times. In comparison, when the pump pulses are centered at 3400 cm\(^{-1}\), the lineshape of the same transition looks more inhomogeneous, as shown in chapter 4 (appendix 4.A.) [32]. The spectral diffusion timescale for a vibration can be obtained by monitoring the decay of center line slope in that particular vibration. We use 3200-3450 cm\(^{-1}\) region of the spectra, corresponding to the O—H stretch vibration of the bulk-like water molecules, to find the center line at all waiting times. Figure 5-3A shows the center lines of bulk-like O—H stretch bleach features in the BB 2DIR spectra of H\(_2\)O and 7M NaOH at different waiting times. The slope of the center line is found to decay with a timescale of 128±20 fs and 241±20 fs in H\(_2\)O and 7M NaOH respectively. Spectral diffusion timescale of O—H stretch vibration in H\(_2\)O was found to be 175 fs from BB 2DIR
Figure 5-3: (A) BB 2DIR spectra of H₂O and 7M NaOH at different waiting times. Black lines on the spectra show the center lines of the O—H stretch bleach feature. (B) Decay of the slope of center line shown in (A). The decay timescales are 128±20 fs and 241±20 fs for H₂O and 7M NaOH, respectively, which are the spectral diffusion timescale.

spectra when the pump pulse is centered at 3400 cm⁻¹ [32]. With the pump center frequency is shifted to the red, we observe a faster decay largely due to the inherent homogeneity of the lineshape due to convolution of the pump spectrum with the response function. The
spectral diffusion timescale of bulk-like O—H stretch vibration in 7M NaOH (241 fs) is slower than that of H₂O, largely due to slowdown of overall dynamics as a result of higher viscosity of the solution.

As a function of waiting time, we observe the diagonal feature corresponding to asymmetric O—H stretch vibration of solvating water molecules in 7M NaOH to shift its center in ω₁. A similar shift is observed for the induced absorption feature in the ω₃=3600-3650 cm⁻¹ region. This feature is essentially a signature of the “thermal-difference” spectrum. In order to quantify these shifts, we take slices from the BB 2DIR spectra of 7M NaOH along ω₁, keeping ω₃ fixed at certain values (Fig. 5-4A and 5-4B). Such a slice of BB 2DIR spectra provides us information about detecting a vibration at a fixed frequency ω₃, irrespective of its excitation, after a waiting time τ₂. We have taken ω₃ slices at three different frequencies: 2850 cm⁻¹, 3378 cm⁻¹ and 3610 cm⁻¹; in order to quantitatively determine the shifts in center frequency of the corresponding vibrational features in ω₁ as a function of τ₂ (Fig. 5-4B).

At the bottom of Fig. 5-4B, we have ω₃ slices at 2850 cm⁻¹ as a function of waiting time. At early waiting times (τ₂<250 fs), the slices show a bleach in the lower ω₁ region and an induced absorption in the higher ω₁ region, indicating we detect a diagonal bleach of asymmetric O—H stretch vibration when we excite them at lower frequencies. On the contrary, on excitation of the O—H stretch vibration of bulk-like water molecules, we observe an induced absorption feature at 2850 cm⁻¹. At longer waiting times (τ₂>500 fs), the induced absorption is absent due to completion of vibrational relaxation of O—H stretch of bulk-like water molecules. The “thermal-difference” bleach signature corresponding to asymmetric O—H stretch vibrations is present at longer waiting times.
**Figure 5-4:** (A) BB 2DIR spectra of 7M NaOH at $\tau_2=100$ fs. $\omega_3$ slices from the spectra are taken at frequencies marked by the dotted lines, for all waiting times. (B) $\omega_3$ slices of BB 2DIR spectra of 7M NaOH at three different frequencies: 2850 cm$^{-1}$ (bottom), 3378 cm$^{-1}$ (middle) and 3610 cm$^{-1}$ (top). (C) (red circles) Shift of the bleach peak in the 2850 cm$^{-1}$ slice as a function of waiting time; (blue square) peak position of the bleach feature in the 3378 cm$^{-1}$ slice and (green diamonds) shift of the induced absorption peak in the 3610 cm$^{-1}$ slice. The shifting peaks are fit to a single exponential function.

There is an isosbestic point in this slice ($\omega_1=3025$ cm$^{-1}$), which is usually interpreted as a
sign of one peak increasing and the other decaying. However, in our case, the bleach of asymmetric O—H stretch vibration and the induced absorption of bulk-like O—H stretch vibration are not directly related. In other words, one does not grow at the expense of other’s decay. In order to precisely determine the peak of the bleach feature, we fit the slices at each waiting time to a sum of two Gaussians. From the fit, we find that the peak frequency of this bleach blueshifts by ~200 cm$^{-1}$ on 180 fs timescale (Fig. 5-4C).

In the middle of Fig. 5-4B, $\omega_3$ slices at 3378 cm$^{-1}$ are shown. We observe a single bleach feature in these slices whose peak frequency does not change much with waiting time. This bleach feature corresponds to O—H stretch of bulk-like water molecules and is peaked in the 3200 cm$^{-1}$ region at all waiting times. Ideally, this peak should have been observed near 3400 cm$^{-1}$. However, due to a redshifted pump pulse compared to O—H stretch vibration of bulk-like water molecules, we see a resultant peak close to the pump center frequency. At longer waiting times, “thermal-difference” bleaches arising from different O—H stretches are centered almost at the same frequency in $\omega_1$ (Fig. 5-4B, bottom and middle). This suggests that the asymmetric stretch vibration loses its identity at longer waiting times. In other words, as a function of waiting time, the excited asymmetric stretch vibration gets to experience the environment of bulk-like O—H stretch vibration. The bulk-like O—H stretch vibration also spectrally diffuse on 241 fs timescales. As a result, an excited bulk-like O—H stretch also gets to explore the environment on similar timescale. One plausible explanation for such observation is vibrational energy transfer between different types of O—H stretches. A vibrational energy transfer on similar timescales would retain no memory of excitation for either kind of O—H stretch vibration. Similar vibrational energy transfer has been observed in case of aqueous acids as well, where bend
vibrations of solvated proton and bulk-like water molecules exchange energy on similar timescales [39].

The \( \omega_3 \) slices at 3610 cm\(^{-1} \) also shows a similar blueshift in the peak frequency of the induced absorption feature due to “thermal-difference” effect compared to bleach of asymmetric O—H stretch vibration (Fig. 5-4B top). This blueshift occurs on 160 fs timescale. Eventually, at longer waiting times, the induced absorption is peaked at the same frequency as the bleach of bulk-like O—H stretch vibrations. Had there been no vibrational energy exchange between bulk-like and asymmetric O—H stretch vibrations, one would have expected this induced absorption feature to retain two separate peaks in \( \omega_1 \). Instead, a single peak is expected in a scenario where two types of O—H stretch would not retain their identity. Timescale of the blueshift of the peak is similar to shift of the bleach of asymmetric stretch vibration, indicating a self-consistent explanation for a vibrational energy transfer case.

In order to study the relaxation behavior of the vibrations present in the system, we have performed TA spectroscopy. Ideally, one would like to get information about vibrational relaxation from BB 2DIR spectra itself. However, due to difficulty in acquiring large amount of BB 2DIR data for that purpose, we use TA spectroscopy. TA spectra can be obtained from the BB 2DIR spectra by integrating along \( \omega_1 \), thereby sacrificing resolution across the excitation frequency axis.

Figure 5-5 shows TA spectra of neat water and aqueous NaOH solutions of concentrations ranging from 3M to 7M, for waiting times up to 1 ps. Even though the bandwidth of our pump pulses are 400 cm\(^{-1} \), we center the pump pulses at 3400 cm\(^{-1} \) (blue-pump) to preferentially excite the O—H stretch vibrations of bulk-like water molecules or
Figure 5-5: (A) and (B) Dispersed transient absorption spectra of H₂O and aqueous NaOH solutions of concentrations ranging from 3M to 7M, up to a waiting time of 1ps with varying pump pulse center frequency. The pump spectrum is shown in blue (A) and red (B) shaded bars corresponding to center frequencies of 3400 cm⁻¹ and 3100 cm⁻¹ respectively. The Normalized FTIR spectra of H₂O and aqueous NaOH solutions are shown on the side. The region of detection frequency below 2200 cm⁻¹ is multiplied by a factor of 5 in (A) and by a factor of 3 in (B) to enhance the spectral features. The asterisk marks the region of spectral interference by atmospheric CO₂.

at 3100 cm⁻¹ (red-pump) to preferentially excite the asymmetric O—H stretches of the water molecules solvating the OH⁻ ion. As a result, features due to the solvated hydroxide ion are more prominent in red-pump TA spectra. To highlight the differences, we compare
Figure 5-6: (A) Slices from transient absorption spectra of H₂O and 7M NaOH taken at τ₂ = 100 fs and τ₂ = 6 ps. These slices are normalized to the maximum in the 3600-3800 cm⁻¹ region of the spectra. (B) Comparison of transient absorption spectra at τ₂ = 6 ps and thermal difference spectra of H₂O and 7M NaOH, where the temperature difference is ~3°C from the room temperature. Here, the spectra are normalized to the absolute maximum change in absorbance in the entire spectral region. The asterisk marks the region of spectral interference by atmospheric CO₂.

slices of the TA spectra at two different waiting times in Fig. 5-6A. Most notably, the bleach of asymmetric O—H stretch vibrations of solvating water molecules at 2850 cm⁻¹ is stronger in red-pump spectra as well as the induced absorption feature below 2200 cm⁻¹. As TA spectra detects response from all the excitation frequencies, the bleach of the asymmetric O—H stretch vibration is overlapped with the induced absorption of the O—H stretch from bulk-like water molecules. As seen from the spectra in Fig. 5-5, relaxation of the induced absorptions occurs within the first 300 fs in H₂O and 200 fs in aqueous NaOH solutions, which are significantly faster than the 1-2 ps reorganization of hydrogen
bonds in the liquid. After 1 ps, the TA spectra closely resemble the difference FTIR spectrum for a small temperature rise for all the samples (ΔT=2-3°C), as seen from Fig. 5-6B. These observations indicate that ultrafast vibrational relaxation processes involving all vibrational degrees of freedom are present and that the relaxation processes of water and solvated OH⁻ ion are closely related.

![Figure 5-7: First two components of CSVD obtained from red-pump TA spectra of H₂O (A) and 7M NaOH (B). The left column shows the spectral components and the right column shows the time dependence of the components. The asterisk marks the region of spectral interference by atmospheric CO₂.](image)

Singular value decomposition (SVD) of TA spectra decomposes it into various spectral components with their associated timescales. Singular value of these components determine their contribution to the overall data. We employ SVD analysis to the red-pump TA spectra of neat water and 7M NaOH solution. For both of them, we obtain two
components as chief contributor to the experimental data, a long waiting time and a short waiting time spectra. We constrain the long waiting time spectral component to be identical to the TA spectra at 6 ps waiting time for the corresponding concentration and recalculate the first two components of SVD, also known as constrained SVD (CSVD). As shown in Fig. 5-7A, such decomposition works great for neat water as we obtain a short waiting time spectra with decay timescale of 230 fs and a long waiting time spectra with a growth timescale of 738 fs, indicating neat water to be a system with two dynamical components. Similar two component decomposition has been found from the blue-pump TA spectra with 275 fs and 722 fs timescales respectively. The short waiting time component in 7M NaOH can be fit well to a single exponential yielding a 235 fs timescale (Fig. 5-7B). However, the long waiting time spectral component is associated with a growth that cannot be fit to a single exponential. A bi-exponential fit results two timescales of 275 fs and 1.55 ps. The longer timescale component can possibly be due to a long lived solvated hydroxide species that retains its identity beyond the relaxation of most other vibrations in the system.

Such CSVD analysis of TA spectra are useful to obtain spectral features and their associated timescales. However, such an analysis cannot separate spectral features with similar timescales. Vibrational relaxation of different types of O—H stretch vibrations and H-O-H bend vibrations are not markedly different. Hence, CSVD cannot separate them efficiently. Eventually the timescale we obtain for the CSVD spectral components only provide us an estimate of the vibrational relaxation timescales of all the spectral features that show up in a particular component.

In order to obtain vibrational relaxation timescale for individual vibrations, we take frequency slices of red-pump TA spectra, as shown in Fig. 5-8. To avoid pulse overlap
effects, we fit the time traces only after 100 fs waiting time in the O—H stretch region and after 150 fs below 2000 cm\(^{-1}\), accounting for the chirp in the BBIR pulse. These time traces are fit to exponentials for extracting the timescales. A single exponential fit does not work well for these time traces and therefore a bi-exponential fit is used.

\[ A \times H_2O \quad \quad \quad 7M \text{NaOH} \]

\[ B \]

Figure 5-8: Time traces at \(\omega_3 = 2920\) cm\(^{-1}\) (A) and \(\omega_3 = 1750\) cm\(^{-1}\) (B) of H\(_2\)O and 7M NaOH obtained from the TA spectra shown in Fig. 5-5.

Figure 5-8A shows vibrational relaxation of the O—H stretch induced absorption in water at 2920 cm\(^{-1}\). It is fit to a bi-exponential with timescales of 250 fs and 1.1 ps. On the other hand the time trace at the same frequency from the 7M NaOH spectra fits to a bi-exponential fit function with 220 fs and 1.9 ps timescales. For 7M NaOH, this induced absorption feature is overlapped by the bleach of asymmetric O—H stretch vibration. That
is one of the reasons behind bi-exponential decays of the time traces. However, O—H stretch vibrations can have somewhat different vibrational relaxation timescale depending on its hydrogen bond strength. As TA spectra is not resolved across excitation frequencies, a combination of different timescales may be present in a time trace, resulting bi-exponential decay. A similar bi-exponential decay is also observed in the time traces taken at 1750 cm$^{-1}$, as shown in figure 5-8B. The fast timescale is 180 fs for neat water and 150 fs for 7M NaOH, whereas the slow timescale varies from 850 fs in neat water to 1.8 ps in 7M NaOH. It is clear from these observations that we have relaxation of the induced absorption features in TA spectra of neat water and 7M NaOH on 150-300 fs timescale. At the same time, a >1.5 ps timescale in the 7M NaOH spectra might point towards persistence of a hydroxide species for a long period of time. However, being more quantitative about the lifetime of different vibrations is not possible from this data due to overlap of spectral features.

Apart from providing information about the vibrational lifetime, polarization dependent TA spectra also indicates about the delocalized nature of the vibrations present in aqueous NaOH solution. Figure 5-9A shows red-pump TA spectra of 7M NaOH in parallel and perpendicular polarization geometry and Fig. 5-9B shows a difference between them. The difference spectra is proportional to the rotational anisotropy of the vibrational features. It has been shown for neat water that the O—H stretch vibration is polarized in nature, whereas the H-O-H bend vibration is depolarized [32]. This is indicative of the fact that O—H stretch vibrations are delocalized in nature but polarized. However, the coupled bend vibrations are depolarized due to random direction of their transition dipoles with respect to the stretch dipoles. Similar to neat water, we observe that in 7M NaOH (Fig.
5-9B), the spectral region of 1600-3000 cm\(^{-1}\) is sharply polarized which decays in <100 fs, within our pulse width. At the same time the difference spectrum does not show any ridges.

![Figure 5-9](image)

**Figure 5-9:** (A) Polarization dependent TA spectra of 7M NaOH using pump pulses centered at 3100 cm\(^{-1}\), normalized to the maximum of the parallel surfaces. They are plotted on the same scale in this figure. (B) Parallel minus perpendicular difference TA spectra of 7M NaOH. The frequency region below 2200 cm\(^{-1}\) is multiplied by a factor of 5 to highlight the spectral features. The asterisks mark spectral interference due to atmospheric CO\(_2\).

in the H-O-H bend region (1630-1700 cm\(^{-1}\)), indicating a depolarized bend vibration. Therefore, we can conclude that the O—H stretch vibrations, specially the asymmetric stretch vibration in aqueous hydroxides and other spectral features in 1600-3000 cm\(^{-1}\) region are delocalized in nature. This observation is in accordance with our previous
finding that the O—H stretch vibrations in solvated hydroxide ions are delocalized over 4-8 water molecules [35].

5.4. Conclusions and Future Work:

Analysis of waiting time dependent BB 2DIR spectra and TA spectra provide us insight about the vibrational dynamics in aqueous hydroxide alongside providing signature of fast proton movement in the system. The vibrations in neat water and aqueous hydroxide solution are delocalized in nature, supported by the polarization dependent TA data. At the same time, these vibrations relax on a timescale of 150-300 fs, as seen from the TA spectra. Analysis of the BB 2DIR spectra shows that O—H stretch vibrations of bulk-like water molecules spectrally diffuse within 220 fs. Asymmetric O—H stretch vibrations of water solvated OH− ions also lose its excitation memory on 180 fs timescale. Similar to these two features, an induced absorption feature in the 3610 cm−1 region, resembling the “thermal-difference” spectra also shifts in frequency on 160 fs timescale to align to the bleaches of different O—H stretches at longer waiting time. These timescales indicate that vibrational energy is transferred between bulk-like and asymmetric O—H stretch vibration, leading to loss of excitation memory for both within 180-220 fs.

However, our experiments does not provide much insight on the long timescale proton transport process. In order to study changes in the vibrations for longer waiting times, we require longer lived vibrations. As the vibrations in our system relax on hundreds of fs timescale, it is tough to study exchanges between them on ps timescale. One way of getting around this problem is to use isotope diluted solutions, so that a particular proton can be tagged to study PT alongside slowing down the vibrational relaxation process.
Ultrafast IR spectroscopy of isotope diluted aqueous NaOH solution has suggested a 3 ps timescale for successful PT [13]. However, in such scenarios, we are no longer sensitive to the vibrational delocalization effects and hence its importance in PT is not taken into account in studies using isotope diluted samples.

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References:


5.A. Appendix: Waiting time dependent BB 2DIR spectra of H$_2$O and 7M NaOH

![Figure 5-A1](image)

**Figure 5-A1:** BB 2DIR spectra of H$_2$O and 7M NaOH/H$_2$O at waiting times ranging from 100 fs to 3000 fs. The pump pulse center frequency is at 3100 cm$^{-1}$ for all the spectra. The spectra are normalized to the absolute maximum peak intensity in the 3200-3600 cm$^{-1}$ region of detection frequency ($\omega_1$). The regions below 2200 cm$^{-1}$ in detection frequency ($\omega_3$) of the spectra have been multiplied by a factor of 15 to highlight the spectral features. The asterisk marks the region of spectral interference by atmospheric CO$_2$. 

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Chapter 6

A Phenomenological Model for Calculating 2DIR Spectra of Strongly Hydrogen Bonded Systems

6.1. Introduction:

Infrared (IR) spectroscopy offers information about molecular vibrations in terms of their characteristic frequencies, intensities and lineshapes. Molecular vibrations, in general, are anharmonic in nature causing fundamental and subsequent overtone transitions to occur at different frequencies. Information about anharmonicities of molecular vibrations can be obtained from the induced absorption features in the 2DIR spectra, which is otherwise unattainable from linear IR spectra [1–3]. For molecular vibrations like the C=O stretch in metal carbonyls or coupled C=O stretch with ring vibrations in nucleic acid bases, the width of the bleach and induced absorption features in their 2DIR spectra are usually similar, typically a few tens of wavenumbers [3–5].

However, distinct signatures are observed in the IR spectra of strongly hydrogen bonded systems, particularly for O—H···O and O—H···N hydrogen bonds, where its energy is in excess of 3.5 kcal/mol. Hydrogen bond formation causes frequency shifts and
broadening of the spectral features. For systems like carboxylic acid dimers, DNA, aqueous solutions and ice, the linear absorption band of some intramolecular vibrations (O—H and N—H stretch vibrations, for example) can be spread across several hundred wavenumbers [6–21]. Qualitatively, such broad spectral features in these systems originate in strong coupling between intra- and intermolecular vibrations. As a result, a progression of intermolecular vibration assisted intramolecular vibrational transitions can take place, yielding a broad spectral lineshape.

With the development of broadband IR (BBIR) pulses for 2DIR experiments, some interesting spectral features have surfaced in the broadband 2DIR (BB 2DIR) spectra of strongly hydrogen bonded systems, which could not be observed previously due to bandwidth limitations. Figure 6-1 shows BB 2DIR spectra at a waiting time of 100 fs for three such strongly hydrogen bonded systems: neat liquid water, 7M NaOH solution and 5M HCl solution. In these spectra, a diagonal bleach feature corresponding to O—H stretch vibrations (3200-3500 cm\(^{-1}\)) is accompanied by an unusually broad induced absorption, spreading across >1700 cm\(^{-1}\). The center of this induced absorption feature is redshifted from the center of the diagonal bleach feature by ~450 cm\(^{-1}\), a value too large to be rationalized as a result of anharmonicity alone. Another induced absorption, resembling a feature in the “thermal-difference” spectra, shows up at higher frequencies compared to the O—H stretch bleach, almost at the time of excitation. The waiting time dependences of these features are also unique. The lower frequency broad induced absorption decays on 200-300 fs timescale and the high frequency induced absorption grows on 500-750 fs, as shown in Chapter 5. These spectral features are present in medium strength hydrogen bonded systems like N-methyl acetamide [22], however, they are most prominent for
aqueous systems where the hydrogen bonds are stronger. We aim to construct a model that reproduces the features in the BB 2DIR spectra of aqueous solutions.

**Figure 6-1:** BB 2DIR spectra of H$_2$O, 7M NaOH and 5M HCl taken at a waiting time of 100 fs. The spectra are normalized to the absolute maximum peak intensity in the 3200-3600 cm$^{-1}$ region of detection frequency ($\omega_3$). The regions below 2200 cm$^{-1}$ in detection frequency ($\omega_3$) of the spectra have been multiplied by a factor of 10 to highlight the spectral features. The asterisk marks the region of spectral interference by atmospheric CO$_2$. The green and black shaded regions indicate the induced absorption features under consideration, with arrows of corresponding colors pointing towards the peak of these features.

Broadening of IR spectral lineshape in these systems has been described in light of strong coupling between intra- and intermolecular vibrations [6,8–11,23–26]. For aqueous systems, we are largely concerned with the transitions arising from anharmonic O–H
stretch vibrations that are coupled to a hydrogen bond displacement or other intermolecular coordinate. In this chapter, we shall explore different forms and approximations required for a two-dimensional model, consisting of an O—H stretch and an O---O hydrogen bond vibration, to yield BB 2DIR spectral signatures observed in the experiments. Even though our model system resembles an R—O—H----O hydrogen bonded dimer, the methods are generally applicable to any strongly hydrogen bonded systems. There are a number of existing models for R—O—H----O hydrogen bonds which takes into account coupling between O—H and O---O modes in different ways starting from harmonic coupling in displaced harmonic oscillator model to empirical anharmonic coupling in Lippincott-Schroeder model [6–12,17–21,23–33]. Many of these models use adiabatic separation between the intra- and intermolecular vibrations, where the intermolecular coordinate is considered as a parameter for calculating energy levels of the intramolecular vibration. Subsequently, the energy levels of the intermolecular vibrations can be determined at each intramolecular energy level. Thus, the eigenstates of the two-dimensional potential can be represented by separate quantum numbers corresponding to intra- and intermolecular modes. Fermi-resonance in these systems are also proposed to play an important role in broadening of the spectral features [34,35]. We shall use some of the existing models to explore their strengths and weaknesses, eventually formulating one that is able to reproduce the BB 2DIR spectral features self-consistently.

Such a two-dimensional model provides clear molecular level insight in the case of a hydrogen bonded dimer. However, for the aqueous systems in discussion, the vibrations are delocalized in nature. In such situations, a two-dimensional model is insufficient for obtaining detailed molecular level understanding of the spectral features. Instead, our goal
is to find out the necessary conditions for such a model consisting of coupled intra- and intermolecular vibrations to yield the observed BB 2DIR spectral signatures and the possible microscopic origin of such scenarios in case of delocalized vibrations.

6.2. Methods:

In this chapter, we use a system consisting of two coupled vibrational modes: one resembling a high frequency intramolecular vibration and the other a low frequency intermolecular vibration, as expressed by the Hamiltonian in Eq. 6-1. The coupling between these vibrations varies from being linear to nonlinear in the vibrational coordinates across different models.

\[ H_{\text{system}} = \frac{p^2}{2\mu} + \frac{p^2}{2M} + V_{\text{intra}}(q) + V_{\text{inter}}(Q) + V_{\text{coupling}}(q,Q) \]  

(6-1)

Here, the lowercase variables correspond to intramolecular vibration and the uppercase ones correspond to intermolecular vibration. The form of the potential energy terms varies across the different models used.

For calculation of BB 2DIR spectra, we require the transition frequencies and transition dipoles for the system under consideration. For specific forms of the potential energy terms in the Hamiltonian (Eq. 6-1), we obtain the eigenstates of the system by solving the Schrödinger equation using the discrete variable representation (DVR) method with particle-in-a-box basis functions [36]. For some models, we consider adiabatic separation of the intra- and intermolecular vibrational coordinates. In these cases, we first solve the one-dimensional Schrödinger equation along the intramolecular coordinate using the intermolecular coordinate as a parameter. These calculations yield the energy levels of
the intramolecular mode as a function of intermolecular coordinate. Finally we solve the one-dimensional Schrodinger equation for the intermolecular vibration at each level of intramolecular mode to end up with the eigenstates of the entire system. In some other scenarios, where no adiabatic separation between the coordinates is involved, we solve the two-dimensional Schrodinger equation exactly to obtain the system eigenstates.

We consider the dipole operator to be a function of the intramolecular coordinate only, which is known as Condon approximation. For strongly hydrogen bonded aqueous systems, Condon approximation is not the most appropriate [37,38]. As our primary focus is to qualitatively reproduce the spectral features in the BB 2DIR spectra, we use this approximation to make our calculations inexpensive yet insightful. The wavefunctions of the system, with mixed intra- and intermolecular character, are used to calculate the transition dipoles ($\mu_i = \langle i | \mu(q) | j \rangle$, where $i$ and $j$ are eigenstates of the system). As the calculations are performed at finite temperatures, few of the lowest energy eigenstates of the system have significant equilibrium population. These states constitute a ground state manifold from which fundamental transitions occur. Dipole allowed transitions can occur from these states to multiple eigenstates of the system owing to varying degrees of intramolecular characters in them, constituting the first excitation manifold. Similarly second and higher excitation manifolds contain multiple eigenstates of the system.

Different excitation pathways contributing to the BB 2DIR spectra for systems described by the Hamiltonian in Eq. 6-1, needs inclusion of two eigenstates at each excitation manifold, in general. We term them as “4-level systems” for the purpose of such calculations, as each of the pathways can involve up to 4 different eigenstates of the system. All possible transitions between the energy levels in different manifolds pertinent to BB
2DIR spectra can be taken into account by several such 4-level systems. In the BB 2DIR experiments, we only detect the rephasing and non-rephasing signals. Therefore, in calculation of the third-order nonlinear response functions for the BB 2DIR spectra, we consider these two types of pathways only. For book-keeping purposes, we represent the pathways as double-sided Feynman diagrams [1], as shown in Fig. 6-2.

### Non-rephasing

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### Rephasing

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**Figure 6-2:** Double-sided Feynman diagrams for rephasing and non-rephasing contributions to the third-order nonlinear response functions. The numbers 0, 1 and 2 in these diagrams denote ground, first and second excitation manifold, respectively. The indices (a, b, c and d) correspond to eigenstates of the system. For a 4-level system like this, we need to involve 4 such eigenstates across different manifolds. The roman numbers corresponding to each diagram refers to the response function term in Eq. 6-2, with an asterisk denoting complex conjugate.
Third-order nonlinear response functions for rephasing and non-rephasing pathways are calculated using the dephasing function formalism developed by Sung and Silbey [39] and later used by Fecko et al [40], as discussed in detail in chapter 2. For this purpose, we consider the system represented by the Hamiltonian in Eq. 6-1 to be linearly coupled to a harmonic bath, leading to fluctuation of the transition energies that can be described by Gaussian statistics. This is known as the second cumulant approximation. The only input we need is a correlation function describing the fluctuations in transition energies, apart from the transition frequencies and dipoles, as shown in Eq. (6-2)-(6-4). For the calculations shown in this chapter, we are interested in reproducing the spectral features of BB 2DIR spectra. Therefore, to keep the calculations in their simplest form, we do not incorporate any phenomenological population relaxation.

\[
\begin{align*}
R_1(\tau_1, \tau_2, \tau_3) & = \sum_{abcd} P_{ab} \mu_{ab} \mu_{cd} e^{-i\omega_{ab} \tau_1} e^{-i\omega_{cd} \tau_2} e^{-i\omega_{ad} \tau_3} F_{abcd}^{(1)} (\tau_3, \tau_2, \tau_1) \\
R_2(\tau_3, \tau_2, \tau_1) & = \sum_{abcd} P_{a} \mu_{ab} \mu_{cd} e^{-i\omega_{ab} \tau_1} e^{-i\omega_{cd} \tau_2} e^{-i\omega_{ad} \tau_3} F_{abcd}^{(2)} (\tau_3, \tau_2, \tau_1) \\
R_3(\tau_3, \tau_2, \tau_1) & = \sum_{abcd} P_{a} \mu_{ab} \mu_{cd} e^{-i\omega_{ab} \tau_1} e^{-i\omega_{cd} \tau_2} e^{i\omega_{ad} \tau_3} F_{abcd}^{(3)} (\tau_3, \tau_2, \tau_1) \\
R_4(\tau_3, \tau_2, \tau_1) & = \sum_{abcd} P_{ab} \mu_{ab} \mu_{cd} e^{-i\omega_{ab} \tau_1} e^{i\omega_{cd} \tau_2} e^{i\omega_{ad} \tau_3} F_{abcd}^{(4)} (\tau_3, \tau_2, \tau_1)
\end{align*}
\]

(6-2)

Where, a, b, c and d are indices for eigenstates of the system; \(\omega_{pq}\) and \(\mu_{pq}\) are transition frequencies and transition dipoles, respectively. The dephasing functions, \(F_{\\nu=0}^{(n)}(\tau_3, \tau_2, \tau_1)\) are defined in terms of energy gap correlation functions of different excitation manifolds as follows:
\[-\ln \left[F_{abcd}(\tau_3, \tau_2, \tau_1)\right] = h_{bb}(\tau_3) + h_{cc}(\tau_2) + h_{dd}(\tau_1) + h_{bc}(\tau_3, \tau_2)\]
\[+ h_{cd}^+(\tau_3, \tau_2) + f_{bd}(\tau_3, \tau_1; \tau_2)\]
\[-\ln \left[F_{abcd}^{(2)}(\tau_3, \tau_2, \tau_1)\right] = \left[h_{cc}(\tau_3)\right] + \left[h_{bb}(\tau_2)\right] + h_{dd}(\tau_3 + \tau_2 + \tau_1) + \left[h_{bc}(\tau_3, \tau_2)\right] + h_{cd}^+(\tau_3 + \tau_2 + \tau_1; \tau_2)\]
\[+ f_{bd}(\tau_3, \tau_3 + \tau_2 + \tau_1; \tau_2)\]
\[-\ln \left[F_{abcd}^{(3)}(\tau_3, \tau_2, \tau_1)\right] = \left[h_{bb}(\tau_3)\right] + h_{cc}(\tau_3 + \tau_2) + h_{dd}(\tau_1) + h_{cd}^+(\tau_3 + \tau_2, \tau_1)\]
\[-f_{bd}^-(\tau_3, \tau_3 + \tau_2; \tau_1) - f_{bd}(\tau_3, \tau_1; \tau_2)\]
\[-\ln \left[F_{abcd}^{(4)}(\tau_3, \tau_2, \tau_1)\right] = h_{cc}(\tau_3) + h_{dd}(\tau_2 + \tau_1) + \left[h_{bb}(\tau_3 + \tau_2)\right] - h_{bc}(\tau_3, \tau_3 + \tau_2)\]
\[+ h_{cd}^+(\tau_2 + \tau_1, \tau_3) - f_{bd}^-(\tau_2 + \tau_1, \tau_3 + \tau_2; \tau_3)\]  
\[(6-3)\]

Where:

\[h_y(t) = \int_0^t dt_2 \int_0^t dt_1 C_{ij}(t_2 - t_1)\]
\[h_y^+(\tau_2, \tau_1) = \int_0^t dt_2 \int_0^t dt_1 C_{ij}(t_2 \pm t_1)\]
\[f_{ij}^+(\tau_2, \tau_1; \tau_3) = \int_0^t dt_2 \int_0^t dt_1 C_{ij}(t_2 \pm t_1 + t_3)\]  
\[(6-4)\]

The total third-order nonlinear response function can be obtained in time domain from Eq. 6-5.

\[R^{(3)}(\tau_3, \tau_2, \tau_1) = \left(\frac{i}{\hbar}\right)^3 \sum_{i=1}^4 [R_i(\tau_3, \tau_2, \tau_1) - R_i^*(\tau_3, \tau_2, \tau_1)]\]  
\[(6-5)\]

We Fourier transform the total response function with respect to \(\tau_1\) and \(\tau_3\) to get the frequency domain response function. Assuming delta function pulses, the spectra are proportional to the frequency domain response functions. All the BB 2DIR spectra shown in this chapter are calculated at \(\tau_z = 0\) fs, as we are primarily interested in reproducing the spectral features observed in the early waiting time BB 2DIR experimental spectra.
6.3. Results and Discussion:

BB 2DIR spectra are calculated for a two-dimensional model Hamiltonian described by Eq. 6-1. The parameters for the intramolecular and intermolecular vibrational potentials are chosen to resemble an O—H stretch vibration and an O---O vibration, respectively. We have examined a few models where the form of the potential energy functions are changed from harmonic to strongly anharmonic along with changes in the form of the coupling, to establish the minimum requirements of such a model to describe the spectral features.

6.3.1. Displaced Harmonic Oscillator Model:

A displaced harmonic oscillator model (DHO) is one of the simplest cases that considers a high frequency transition to be bilinearly coupled to a low frequency harmonic vibration. It has been extensively used in case of vibronic spectroscopy where an electronic transition in influenced as a result of coupling to a vibrational motion of the nuclei [11,41]. A similar scenario can be considered to describe coupling between a high frequency intramolecular and a low frequency intermolecular vibration in the context of vibrational spectroscopy of hydrogen bonded systems. Such description has been used qualitatively to describe the features in transient absorption experiments of carboxylic acid dimer systems [12,30–32].

The DHO model considers adiabatic separation between low and high frequency vibrations. The potential energy for the intermolecular vibration is harmonic at all levels of the intramolecular vibration with the same curvature. Their minima are displaced along the intermolecular vibrational coordinate between two levels of intramolecular vibration.
The extent of this displacement indicates the strength of the coupling between the intra- and intermolecular modes. In such cases, the system has multiple transition dipole allowed states accessible in all the excitation manifolds of the intramolecular vibration due to its coupling to the intermolecular vibration. The number of accessible states in each excitation manifold depends on the strength of the coupling.

\[\text{Figure 6-3: Schematic diagram showing energy levels of an intermolecular vibration in the ground, first and second excited states of an intramolecular vibration. The quantum numbers of the intramolecular vibration, } |n\rangle, \text{ are indicated on the right side. The arrows show dipole allowed fundamental (blue, green and red) and overtone (cyan, dark green and orange) transitions of the intramolecular vibration. Separation between the minima of the potential energy curves for the intermolecular vibration is } d \text{ between two successive states of intramolecular vibration.} \]
Coupling between these two modes is captured by the Huang-Rhys parameter, $D$, defined by Eq. 6-6.

$$D = d^2 \frac{m \omega_0}{2\hbar} \quad (6-6)$$

Where, $d$ is the displacement of the minima of the harmonic potential along the intermolecular coordinate between two levels of intramolecular vibration under consideration, $m$ is the reduced mass and $\omega_0$ is the frequency of the intermolecular vibration. $D$ is a unitless positive number, where $D > 1$ and $D << 1$ corresponds to strong and weak coupling, respectively. We have used 0.1 and 1.1 as two different values of $D$ in two separate calculations, in order to highlight the effects of strong coupling.

In this model, the fundamental and overtone transition frequencies of the uncoupled intramolecular vibration are required. Our choice of these transition frequencies resemble a typical O—H stretch vibration in aqueous medium, with $\omega_{10} = 3400 \text{ cm}^{-1}$ and $(\omega_{21}-\omega_{10}) = 300 \text{ cm}^{-1}$. Parameters for the intermolecular vibration are chosen in conformity with an O---O vibration ($\omega_{\text{low}} = 200 \text{ cm}^{-1}$). In order to calculate transition dipoles for various transitions, we use Condon approximation, where the dipole moment operator only depends on the intramolecular coordinate. The fundamental and overtone transitions of the intramolecular vibration have been considered to have harmonic transition dipoles. Transition dipoles between different states are obtained by weighing the harmonic transition dipoles of the intramolecular vibration with the corresponding Franck-Condon coefficients, i.e. the overlap between the initial and final intermolecular vibrational states.

The third-order nonlinear response functions are calculated in the time-domain using Eqs. (6-2)-(6-4) for all possible pathways described in Fig. 6-2. We have used an
energy gap correlation function, $C_{eg}(t)$, closely resembling the one used for HOD in D$_2$O, shown in Eq. 6-7 with the parameters provided in Table 6-1 [40]. The energy gap correlation function is assumed to be identical for all the energy gaps in consideration, i.e. fluctuation of energy gap due to coupling to a harmonic bath is considered to be uniform across the system. These time-domain response functions are subsequently Fourier transformed to obtain the BB 2DIR spectra.

$$C_{eg}(t) = ae^{-\frac{t}{T_1}} + be^{-\frac{t}{T_2}}[\cos(\Omega t) + (-\frac{1}{T_2\Omega})\sin(\Omega t)]$$

(6-7)

Here, $T_1$ and $T_2$ denote timescale of the two exponential decay components of the correlation function. The decay component with a timescale of $T_2$ is multiplied by an oscillatory component which has a frequency parameter, $\Omega$.

The BB 2DIR spectra shown in Fig. 6-4 are calculated at $\tau_2 = 0$ fs using the parameters mentioned above. The spectra show a progression of diagonal bleach features, 200 cm$^{-1}$ apart corresponding to frequency of the intermolecular vibration. Number of eigenstates accessible to the system increases dramatically when the coupling is strong. Therefore, we observe many more diagonal bleach features for strong coupling as opposed to largely one strong diagonal bleach feature in the weak coupling case. The diagonal bleach features away from the fundamental transition frequency of the uncoupled intramolecular vibration (3400 cm$^{-1}$) intensifies with increase in coupling strength. Alongside it, there are several other bleach features shifted by different multiples of 200 cm$^{-1}$ along both the frequency axes, particularly in the strong coupling spectra. Corresponding induced absorption features to every bleach appear redshifted by 300 cm$^{-1}$ along $\omega_3$, as the anharmonicity ($\omega_{21}-\omega_{10}$) of the intramolecular vibration is 300 cm$^{-1}$. 

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Table 6-1: Parameters used for energy gap correlation function in Eq. 6-7 for the calculations shown in Fig. 6-4.

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<th>Parameter</th>
<th>Value</th>
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<td>b</td>
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</tr>
<tr>
<td>$T_1$</td>
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</tr>
<tr>
<td>$T_2$</td>
<td>120 fs</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>175 cm$^{-1}$</td>
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</tbody>
</table>

Figure 6-4: BB 2DIR spectra at $\tau_2 = 0$ fs calculated for DHO model using the parameters mentioned above. Coupling between the intra- and intermolecular vibration, represented by the Huang-Rhys parameter ($D$), are different for the two spectra. (Left) $D = 0.1$ corresponding to weak coupling and (Right) $D = 1.1$ corresponding to strong coupling.

At $\tau_2 = 0$, ideally all the peaks should be diagonally elongated. However, it is often twisted and at times looks to be anti-diagonally elongated (e.g. diagonal bleach at 3400 cm$^{-1}$ in the strong coupling spectrum). The third order response functions include product of four transition dipoles (Eq. 6-2). The sign of the transition dipoles are dictated by the
sign of the corresponding Franck-Condon factor. For a 4-level system, it is possible to have four different transition dipoles corresponding to the eigenstates involved in certain pathways, leading to an overall negative sign of their product as opposed to the usual positive sign. As the final spectrum is a combination of several such 4-level systems, the peaks can be twisted due to the presence of contribution from opposite signed peaks.

In the DHO model, coupling between intra- and intermolecular vibration gives rise to an array of peaks in the BB 2DIR spectra, equivalent to line broadening in strongly hydrogen bonded system. However, the width of the induced absorption features are not different compared to the bleaches. Thus, this model is insufficient in describing the spectral features observed in the BB 2DIR spectra of aqueous systems. There are a few assumptions involved in DHO model: harmonic potential for intermolecular mode, bilinear coupling between intra- and intermolecular vibration and adiabatic separation between them. We shall take out these assumptions gradually in the subsequent models and study their effects.

6.3.2. Bilinearly Coupled Morse Oscillators:

As the next step in improving the assumptions of DHO model, we choose both the intra- and intermolecular vibration to be anharmonic in nature and represented by two Morse oscillators (Fig. 6-5A). The form of the potential and its parameters are provided in Eq. 6-8 and Table 6-2, respectively.

\[ V_{\text{intra}, \text{baco}}(x) = V_0 (1 - e^{-n(x - x_0)})^2 \]  \hspace{1cm} (6-8)

Where, \( V_0 \) and \( n \) represent the dissociation energy and the anharmonicity parameter for the
potential, respectively and \( x \) is a generalized coordinate with a potential energy minimum at \( x_0 \). Similar to the DHO model, the parameters for the potentials are chosen to represent O—H stretch as the intramolecular vibration and the O---O vibration as the intermolecular vibration.

**Table 6-2:** Morse potential parameters for the intra- and intermolecular vibrations.

<table>
<thead>
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<th>Intramolecular Vibration</th>
<th>Intermolecular Vibration</th>
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<td>( V_0 ) (cm(^{-1}))</td>
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<td>2340</td>
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<td>( n ) (Å(^{-1}))</td>
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<td>1.5</td>
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<td>( x_0 ) (Å)</td>
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<tr>
<td>Fundamental Frequency (cm(^{-1}))</td>
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<td>Overtone Frequency (cm(^{-1}))</td>
<td>3100</td>
<td>191.0</td>
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</tbody>
</table>

Similar to DHO Model, we have chosen a bilinear coupling between the two modes. The form of the coupling is shown in Eq. 6-9.

\[
V_{\text{Coupling}}(q, Q) = kqQ
\]  

(6-9)

The value of the coupling constant, \( k \), is chosen to be 15000 and 25000 cm\(^{-1}\)/Å\(^2\) in two separate cases. Our choice of the coupling parameter is driven by changes in the nature of eigenstates of the system. With stronger coupling, the eigenstates have more mixed intra- and intermolecular character. We increase the coupling parameter only up to a point that does not drastically distort the two-dimensional potential. To compare, we calculate the BB 2DIR spectra for the same vibrational potentials when the modes are uncoupled.
Unlike the DHO model, we avoid making any adiabatic approximation in this model. In order to obtain the eigenstates of the system, we solve the Schrödinger equation exactly for the two-dimensional potential shown in Fig. 6-5B. The transition dipoles are calculated using the wavefunctions obtained for the system with a dipole operator that depends only on the intramolecular coordinate. In the strong coupling regime, the eigenstates of the system cannot be recognized by separate quantum numbers
corresponding to intra- and intermolecular vibration. Thus, we have transitions between all the states with significant intramolecular character.

BB 2DIR spectra have been calculated for this model in an identical fashion as the DHO model, using slightly different parameters for the energy gap correlation function, as shown in Table 6-3. The changes are made in the amplitude of the energy gap correlation function, in order to increase the linewidth of the peaks in the BB 2DIR spectra primarily, which were deliberately kept low in the DHO model to observe the progression of peaks distinctively.

Table 6-3: Parameters for energy gap correlation function described in Eq. 6-7.

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<tr>
<td>Ω</td>
<td>175 cm-1</td>
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</table>

Figure 6-6 shows BB 2DIR spectra at τ2 = 0 fs for this model. When there is no coupling between the modes, the spectra looks similar to a simple 3-level system. It has a diagonal bleach feature at 3400 cm⁻¹, corresponding to the fundamental transition of the intramolecular vibration, and an induced absorption at 3100 cm⁻¹, corresponding to the anharmonically shifted overtone transition of the same vibration. With increase in coupling between the vibrations, new bleach and induced absorption features show up ~200 cm⁻¹ apart from the original peaks, corresponding to the intermolecular vibrational frequency. As a result, the spectral features get broader like the DHO model. In contrast to the DHO model, with stronger coupling, there is a diagonal redshift of the original bleach and
induced absorption features (bleach at 3400 cm\(^{-1}\) and induced absorption at 3100 cm\(^{-1}\)) in this model. However, unlike the spectral features in BB 2DIR spectra of aqueous systems and similar to DHO model, the overall width of bleach and induced absorption features are not markedly different. From this model, we conclude that anharmonicity of the intra- and intermolecular modes are not enough to reproduce the spectral features of aqueous systems, when the coupling between them is still bilinear. We did not make any adiabatic separation between the modes in this model but avoidance of such approximation is not enough to result spectral features similar to aqueous systems.

![Figure 6-6: BB 2DIR spectra at \(\tau_2 = 0\) fs for two bilinearly coupled Morse oscillators corresponding to intra- and intermolecular vibrations. The value of coupling constant, \(k\), is indicated for each spectra in the units of cm\(^{-1}\)/Å\(^2\).](image)

In order to monitor the changes in the intramolecular vibrational potential as a result of coupling to the intermolecular mode, we have taken a slice of the two-dimensional potential (Fig. 6-5B) along the intramolecular coordinate. The intermolecular coordinate is
kept fixed at its value where the two-dimensional potential has a global minimum. As seen from Fig. 6-7, the potential for the intramolecular vibration does not change much on being strongly coupled to the intermolecular vibration, even though the eigenstates of the system have mixed intra- and intermolecular character in the strong coupling regime.

![Graph](image)

*Figure 6-7:* Intramolecular vibrational potential taken as slices from two-dimensional potential in Fig. 6-5B, keeping the value of intermolecular coordinate fixed at 2.8 Å, its value where the two-dimensional potential has a global minimum. The legends indicate the strength of the coupling.

6.3.3. Effect of Fermi Resonance:

Another effect that is often responsible for spectral broadening and is present in strongly hydrogen bonded system is Fermi resonance [34]. Fermi resonance is an effect when the fundamental transition of a bright mode comes in resonance with an overtone or combination band of a dark mode. Due to this resonance, the resultant eigenstates of the system have mixed bright and dark state character. Thus, larger number of eigenstates can be accessed which leads to spectral broadening.
Figure 6-8: Schematic diagram showing stretch-bend Fermi resonance, similar to liquid water. The eigenstates of the system are represented as $|mn\rangle$, where $m$ is the quantum number of stretch vibration and $n$ is that of the bend vibration. The $|10\rangle$ and $|02\rangle$ states are almost degenerate and couples strongly to give rise to two states. The transition dipole of the system has been assumed to depend only on the stretch coordinate and hence $|10\rangle$ is bright and $|02\rangle$ is a dark state. However, Fermi resonance causes both the states arising from $|10\rangle$ and $|02\rangle$ to be bright. Similarly, $|20\rangle$, $|04\rangle$ and $|12\rangle$ can mix to give rise to three states, all bright. The solid and dotted lines correspond to the frequencies of fundamental and overtone transitions.

In order to examine the effects of such resonances on spectral broadening, we calculate BB 2DIR spectra for a system that resembles stretch-bend Fermi resonance in liquid water. In a stretch-bend Fermi resonance, the overtone of bend vibration is in resonance with the fundamental of the stretch vibration. As we primarily excite the O—H stretch vibrations in the experiments, we are concerned about the effects of the overtone of bend vibration in the O—H stretch region. A schematic representation of the scenario is shown in Fig. 6-8 and the parameters are shown in Table 6-4. The BB 2DIR spectra are calculated for this system as before, using an energy gap correlation function with the same form as in Eq. 6-7 and same parameters as in Table 6-3.
Table 6-4: Parameters for stretch-bend Fermi resonance. The parameters are chosen to resemble that of liquid water.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ω₁₀ stretch</td>
<td>3350</td>
</tr>
<tr>
<td>ω₂₁ stretch</td>
<td>3050</td>
</tr>
<tr>
<td>ω₁₀ bend</td>
<td>1680</td>
</tr>
<tr>
<td>ω₂₁ bend</td>
<td>1650</td>
</tr>
<tr>
<td>Coupling</td>
<td>175</td>
</tr>
</tbody>
</table>

Figure 6-9: BB 2DIR spectra at τ₂ = 0 fs for a stretch-bend Fermi resonance system. (Left) When the cubic force constant is forced to be zero, there is no coupling between stretch and bend. (Right) However, once the cubic force constant becomes finite, the BB 2DIR spectrum has several features.

Figure 6-9 compares the BB 2DIR spectra for a stretch-bend Fermi resonance system between two scenarios: one when the cubic force constant is zero and the other when it assumes a finite value. When the cubic force constant is zero, we only observe bleach and anharmonically shifted overtone transition of the O—H stretch vibration (Fig.
Two diagonal bleach features appear when the cubic force constant is finite (Fig. 6-9, left). Two diagonal bleach features appear when the cubic force constant is finite (Fig. 6-9, right), as expected from a stretch-bend Fermi resonance system (transition from ground state to both the states resulted due to coupling between $|10\rangle$ and $|02\rangle$ in Fig. 6-8). These diagonal bleach peaks appears on either side of the uncoupled stretch fundamental (Fig. 6-9). It is accompanied by off-diagonal bleaches of the diagonal peaks. For each diagonal peak, there can be 6 different induced absorptions at different frequencies. A stretch-bend Fermi resonance broadens both the bleach and induced absorption features in the BB 2DIR spectra due to overlap of multiple transitions.

The induced absorption can be broader than bleach for a stretch-bend Fermi resonance system. However, it is not broad enough to explain the width of the features observed in BB 2DIR spectra of aqueous systems. At the same time, this model, unlike the previous ones, can give rise to induced absorption feature at frequencies higher than bleach (the peak at $(\omega_1, \omega_3) = (3480, 3800)$ in Fig. 6-9, right). Although, such an outcome cannot guarantee influence of Fermi resonance, as we shall see in the forthcoming sub-section.

**6.3.4. Nonlinearly Coupled Anharmonic Oscillators:**

The results of all the models discussed so far have some features in common. All of them cause broadening of the intramolecular vibrational feature due to its coupling to an intermolecular vibration. This broadening can be quite large, and therefore, is well suited to explain the observed broadening in the linear IR absorption spectra of strongly hydrogen bonded systems [11,12,30–32]. However, with the emergence of BB 2DIR spectroscopy, we can access the entire mid-IR region of the spectra, which shows striking differences between the widths of bleach and induced absorption features in aqueous
systems. The lower frequency induced absorption feature has a long tail and there is a higher frequency induced absorption, all of which require a self-consistent explanation.

In order to develop such a model, we would build up on the knowledge gathered using the previously described ones. We shall consider both the intra- and intermolecular vibration to be anharmonic in nature. Given the limited success of bilinear coupling models, we shall introduce nonlinear coupling between the oscillators. Such a model was introduced for hydrogen bonded dimers by Lippincott and Schroeder [24,27,28] and subsequently used to describe results of ultrafast IR experiments on ice by Bakker and Hamm [17–19,21,42].

When a two-dimensional model involving a coupled intra- and intermolecular vibration is used to describe the spectroscopy of liquid systems, it is reasonable to assume that the potentials of the vibrations might have some resemblance to infinite potential wells. In particular, we do not expect the intramolecular vibrations to lead to dissociation of a bond in liquids. An asymmetric double-well potential could be a better choice as opposed to dissociative Morse potential in these situations. On the other hand, we shall use both Morse and asymmetric double-well potentials for intermolecular vibrations and compare their outcome. The general form of the potentials are given by Eq. 6-9 and their relevant parameters in Table 5. Our BB 2DIR spectra of neat water and aqueous NaOH solutions show spectral features corresponding to O—H stretches of bulk/bulk-like water molecules and asymmetric stretch vibrations of water molecules solvating the ions. Therefore, we choose parameters of the intramolecular vibrations corresponding to both of these types of O—H stretches, with an objective to compare their outcomes. One-dimensional vibrational potentials are shown in Fig. 6-10 for asymmetric double-well intramolecular modes and
different types of intermolecular modes.

\[
V_{DW_{Intra/Inter}}(x) = V_0^{DW} \left[-a(x-a)^2 + b(x-a)^3 + c(x-a)^4\right]
\]

(6-10)

\[
V_{Morse_{Intra/Inter}}(x) = V_0^{Morse}\left[1 - e^{-n(x-\beta)}\right]^2
\]

(6-11)

Where, \(x\) is a generalized coordinate for the vibrational modes, \(V_0^{DW}\) and \(V_0^{Morse}\) are two constants for the asymmetric double-well and Morse potentials respectively.

**Table 6-5:** Parameters for asymmetric double-well and Morse potentials corresponding to intra- and intermolecular vibrations

<table>
<thead>
<tr>
<th>Double-well O—H stretch (H(_2)O)</th>
<th>Intramolecular O—H stretch (Ag. NaOH)</th>
<th>Intermolecular O—O vibration</th>
<th>Morse (V_0^{Morse}) (cm(^{-1}))</th>
<th>Intermolecular O—O vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>(V_0^{DW}) (cm(^{-1}))</td>
<td>39000</td>
<td>32500</td>
<td>5000</td>
<td>3000</td>
</tr>
<tr>
<td>(a) (Å(^{-1}))</td>
<td>0.95</td>
<td>0.95</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>(b) (Å(^{-1}))</td>
<td>1.2</td>
<td>1.2</td>
<td>0.9</td>
<td>1.5</td>
</tr>
<tr>
<td>(c) (Å(^{-1}))</td>
<td>2.45</td>
<td>2.65</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>(\alpha) (Å)</td>
<td>1.65</td>
<td>1.65</td>
<td>3.4</td>
<td></td>
</tr>
</tbody>
</table>

In this model we introduce nonlinear coupling between the modes and choose the form of the coupling similar to the one introduced by Lippincott and Schroeder [24,27].

\[
V_{Coupling}(q, Q) = V_0^{Coupling}\left[1 - e^{-\eta(Q-q)^2 - 0.92^2/(2(Q-q))}\right]
\]

(6-12)

The value of \(\eta\) has been chosen to be 16.5 throughout the work, as has been used in similar models for ice by Bakker and Hamm [17,21]. The strength of coupling is determined by the value of \(V_0^{Coupling}\). However, very similar results can be obtained by varying \(\eta\). A sample
Figure 6-10: (A) Asymmetric double-well potential for intramolecular vibration resembling two different types of O–H stretches in neat water and aqueous NaOH solutions, respectively. (B) Asymmetric double-well and Morse potentials for the intermolecular vibrations. The parameters for the vibrations are provided in Table 6-5.

two-dimensional potential for a nonlinearly coupled intra- and intermolecular vibration is shown in Fig. 6-11, where, the potential for intra- and intermolecular vibrations are considered to be asymmetric double-well and Morse potential, respectively. It also shows the coupling between the two modes. The coupling term has a minimum along the diagonal and increases along anti-diagonal direction, resulting in a two-dimensional potential with a minimum distorted along the diagonal signifying mixing of the two modes.
**Figure 6-11:** (Left) Two-dimensional potential energy surface for a coupled intra- and intermolecular vibration where the intramolecular potential is asymmetric double-well and the intermolecular vibration has Morse potential. (Right) Contour plot of the coupling term on the same scale as the two-dimensional potential. The parameters for the intramolecular vibration are chosen to represent O—H stretch vibration of neat liquid water and the coupling constant, $V_0^{\text{Coupling}}$, is chosen to be 4000 cm$^{-1}$/Å$^2$.

We solve the Schrödinger equation with and without adiabatically separating the two vibrational modes and observe the impact of this approximation on the calculated BB 2DIR spectra. The adiabatic approximation impacts the results to varying degrees across the choice of different potential forms for the vibrations, as discussed for the individual cases later in this section. Regardless of the adiabatic approximation, we find eigenstates of the system having strongly mixed intra- and intermolecular vibrational character with stronger coupling. As a result, there are numerous dipole allowed transitions in the system, including many induced absorptions at frequencies higher than the bleaches. For calculation of BB 2DIR spectra of these systems, we use the same energy gap correlation function as used in the other models with the parameters provided in Table 3. In the subsequent part of the section, we shall compare the BB 2DIR spectra for different
combinations of potential forms with and without using the adiabatic approximation.

**a) Asymmetric double-well (intramolecular) and Morse (intermolecular) Potentials:**

We choose the intramolecular vibration to have an asymmetric double-well potential alongside a Morse potential for the intermolecular vibration. A comparison of BB 2DIR spectra at $\tau_2=0$ fs is presented in Fig. 6-12 for intramolecular vibrations resembling O—H stretches of water molecules in H2O and asymmetric stretch vibration of solvating water molecules in aqueous NaOH, with variation in the coupling strength. There is no adiabatic separation between the two modes in the calculations shown in Fig. 6-12.

Without any coupling between the vibrations, we observe spectral features similar to a 3-level system with a bleach and induced absorption at respective fundamental and first overtone transition frequencies of the intramolecular vibration. However, with increase in coupling, we start to broaden the diagonal bleach feature as well as the induced absorption feature due to the increase in number of dipole allowed transitions. Eventually, a strong enough coupling can produce induced absorption features at lower frequencies than the bleach extending beyond 2000 cm$^{-1}$, as observed in aqueous systems. Also, it can result in a higher frequency induced absorption compared to the bleaches. Such a feature appears due to mode-mixing assisted dipole allowed transitions and is inherent to the system. Therefore, this model can qualitatively describe all the spectral features observed in the BB 2DIR spectra of aqueous systems.
Figure 6-12: BB 2DIR spectra at $\tau_2 = 0$ fs for a coupled intra- and intermolecular vibration with asymmetric double-well and Morse potentials for the vibrations, respectively. The parameters in (A) and (B) are chosen such that the intramolecular vibration resemble O—H stretch vibration of water molecules in H$_2$O and asymmetric stretch vibrations of solvating water molecules in aqueous NaOH, respectively. The coupling strength is varied by choosing different values for $\nu_0^{\text{Coupling}}$ in Eq. 6-12. In (A), the values for $\nu_0^{\text{Coupling}}$ are 0, 4500 and 6750 cm$^{-1}$/Å$^2$ going from left to right. Similarly in (B), it is 0, 2500 and 4000 cm$^{-1}$/Å$^2$ going from left to right. No adiabatic approximation has been made in these calculations.
Figure 6-13: Slice of two-dimensional potential energy surface along the intramolecular coordinate, keeping the value of the intermolecular coordinate fixed at its value of global minimum. The values of the coupling constant in different cases are as identical to the ones used in Fig. 6-12.

It is interesting to note that asymmetry of the intramolecular potential changes as a function of coupling strength. To highlight this effect, we have taken slices of the two-dimensional potential along the intramolecular coordinate, with the intermolecular coordinate being fixed at its value at the global minimum. Symmetrization of the intramolecular potential occurs due to mode-mixing with increase in coupling strength.

In the previous models, when the coupling was bilinear, the adiabatic approximation did not make much of a difference. In contrast, in this model the adiabatic approximation does not yield spectral features resembling the experiments. For comparison, we have shown BB 2DIR spectra at $\tau_2 = 0$ fs, for an intramolecular vibration resembling asymmetric O—H stretch of water molecules solvating the hydroxide ion in Fig. 6-14. Adiabatic approximation leads to an induced absorption feature that looks very
**Figure 6-14:** Comparison of BB 2DIR spectra with and without the adiabatic approximation. The parameters for intramolecular vibration are chosen to resemble asymmetric O—H stretch vibration of the solvating water molecules in aqueous NaOH, whereas the intermolecular potential is a Morse potential. The adiabatic approximation cannot reproduce the spectral features observed in the experiments and, therefore, is a poor approximation in this case.

Different from the exact calculation. From this observation, we conclude that our BB 2DIR experimental results can be reproduced by a coupled intra- and intermolecular mode only when there is strong enough coupling to generate eigenstates of the system with mixed character. In other words, the adiabatic approximation effectively expresses the system eigenstates with two quantum numbers corresponding to the modes, which in this case is invalid.
b) Asymmetric double-well (both intra- and intermolecular) Potentials:

*Figure 6-15:* (A) Comparison of BB 2DIR spectra where the form of intermolecular potential has been changed. Parameters for the intramolecular potential are chosen to resemble the O—H stretch vibration of the solvating water molecules in aqueous NaOH. (B) A slice through the two-dimensional potential energy surface along the intramolecular coordinate through the global minima of the potential.

To investigate the impact of a particular potential form in the calculated BB 2DIR spectra, we have chosen asymmetric double-well potentials for both intra- and intermolecular vibrations. A comparison of BB 2DIR spectra is presented in Fig. 6-15A, where the intermolecular vibrational potential is changed between asymmetric double-well and Morse potential. The parameters for intramolecular vibration are chosen for asymmetric O—H stretch vibration of water molecules solvating hydroxide ion. Using an
Figure 6-16: Comparison of BB 2DIR spectra with and without adiabatic separation of the modes, where the intermolecular vibration is an asymmetric double-well potential. Similar to Fig. 6-15, the intramolecular potential is an asymmetric double-well whose parameters resemble the O—H stretch vibration of the solvating water molecules in aqueous NaOH. An asymmetric double-well potential can qualitatively reproduce the spectral features. However, we observe multiple peaks in the lower frequency induced absorption, which deviates from the experimental observation. Also, the diagonal bleach peak redshifts significantly compared to the previous cases. Figure 6-15B shows a slice of the two-dimensional potential energy surface along the intramolecular coordinate through the global minimum. Changing the intermolecular potential from Morse to asymmetric double-well changes the depth of the shallower minima significantly and brings the minima closer together. Unlike the previous case, adiabatic separation of intra- and intermolecular
vibrations have limited impact in this case, as seen in Fig. 6-16.

6.4. Concluding Remarks:

We have used a two-dimensional model system consisting of strongly coupled intramolecular and intermolecular vibrational modes to explain the spectral features observed in the BB 2DIR spectra of aqueous systems. We observe a broad induced absorption feature below the diagonal bleach peak and a higher frequency induced absorption in these systems, which are common to many strongly hydrogen bonded systems. These experimental results have only been reproduced when we have strong, nonlinear coupling between intra- and intermolecular vibrations. Bilinear coupling, however strong, does not reproduce the results (Sec. 6.3).

We have chosen an anharmonic potential for the vibrational modes. For the intramolecular vibration, it is chosen to be an asymmetric double-well potential so that we avoid ionizing a bond in the liquid phase. Using a Morse potential for the intermolecular mode, we observe that increase in coupling between the modes gradually symmetrizes the potential, without changing the position of its minimum (Fig. 6-13). Switching to an asymmetric double-well potential for the intermolecular vibration does symmetrize the intramolecular vibrational potential but it also lowers the well depth of the shallower minima and changes the position of the minima (Fig. 6-15B). The BB 2DIR spectra in this case compare poorly with the experimental one. Thus, we conclude that symmetrization of the intramolecular potential is correlated with reproduction of the experimental spectral features. This symmetrization is also observed when two Morse-like oscillators are nonlinearly coupled [17–19,21], as shown by Bakker and Hamm in their work on ultrafast IR spectroscopy of ice.
Such symmetrization of double-well potential is associated with dissociation of a proton in the case of a dimer. In fact, Bakker has argued in favor of such proton transport in liquid water [19]. However, the dissociation energy of O—H bond is ~40000 cm\(^{-1}\) in gas phase. Even though it is likely to decrease in liquid phase, it is unlikely to undergo ionic dissociation in liquid water. It is also important to recall that vibrations in aqueous systems are delocalized in nature. Therefore, the coordinates in our calculation is much likely to represent a collective vibration, similar to normal modes, even though a normal mode picture in aqueous system is found to perform poorly. In the local mode picture, a notion of ionic dissociation can arise due to symmetrization, however, such an implication is quite unphysical for delocalized vibrations. Therefore, the potential energy we use has some resemblance to the free energy, i.e. it has similarities to minimum energy path along a generalized coordinate involving a large number of degrees of freedom. Due to coupling with an intermolecular mode, the minimum energy path represented by the intramolecular mode changes significantly, as shown in the slices of the potential energy surface.

It might be argued that such a two-dimensional model is too simplistic for a multidimensional problem like this. The importance of considering multiple modes has been emphasized particularly in case of explaining the dynamics of such systems [43–46]. Nevertheless, we get a general picture of the requirements of such a two-mode coupled system to yield the experimental results. It is also worth mentioning that explaining the dynamics of the calculated spectral features is somewhat difficult, especially decay and growth of two different induced absorptions. It is possible that some situations like conical intersection might allow non-adiabatic ultrafast vibrational relaxation to happen. To test for such possibilities, it is important to have multiple modes in the calculation. However,
such calculations come with significant computational costs.

It is also worth mentioning that adiabatic separation between intra- and intermolecular vibrations does not work in reproducing the experimental results (Fig. 6-14). Adiabatic separation of the modes still allow the system eigenstates to be represented using two separate quantum numbers. The failure of such approximation indicates a scenario when the eigenstates of the system have so much mixed character that the notion of individual quantum numbers of the modes become invalid. In such situations, many dipole allowed transitions show up, which we eventually observe in our experimental results.

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References:


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**PUBLICATIONS**


(*) Denotes equal contribution.