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**Practical applications of molecular dynamics techniques and time correlation function theories**

Christina Ridley Kasprzyk

*University of South Florida*

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Practical Applications of Molecular Dynamics Techniques and Time Correlation Function Theories

by

Christina Ridley Kasprzyk

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy Department of Chemistry College of Arts and Sciences University of South Florida

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Note to Reader

Note to Reader: The original of this document contains color that is necessary for understanding the data. The original dissertation is on file with the USF library in Tampa, Florida.
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The original research outlined in this dissertation involves the use of novel theoretical and computational methods in the calculation of molecular volume changes and nonlinear spectroscopic signals, specifically two-dimensional infrared (2D-IR) spectra. These techniques were designed and implemented to be computationally affordable, while still providing a reliable picture of the phenomena of interest. The computational results presented demonstrate the potential of these methods to accurately describe chemically interesting systems on a molecular level.

Extended system isobaric-isothermal (NPT) molecular dynamics techniques were employed to calculate the thermodynamic volumes of several simple model systems, as well as the volume change associated with the trans-cis isomerization of azobenzene, an event that has been explored experimentally using photoacoustic calorimetry (PAC). The calculated volume change was found to be in excellent agreement with the experimental result.

In developing a tractable theory of two-dimensional infrared spectroscopy, the third-order response function contributing to the 2D-IR signal was derived in terms of classical time correlation functions (TCFs), entities amenable to calculation \textit{via} classical molecular dynamics techniques. The application of frequency-domain detailed balance
relationships, as well as harmonic and anharmonic oscillator approximations, to the third-order response function made it possible to calculate it from classical molecular dynamics trajectories. The finished theory of two-dimensional infrared spectroscopy was applied to two simple model systems, neat water and 1,3-cyclohexanedione solvated in deuterated chloroform, with encouraging preliminary results.
Chapter 1

Introduction

Recent advances in theoretical techniques and computational technology have allowed the scientific community to gain meaningful insight into interesting chemical phenomena, even matters as complex as the folding pathway of peptides or multidimensional spectroscopy of condensed phases. The synergy of innovative experimental procedures with computational and theoretical investigations yields a microscopic understanding of the structure and dynamics that are difficult to interpret based on experimental results alone. In this dissertation, theoretical approaches to two relevant problems, the measurement of time-dependent molecular volumes and the calculation and interpretation of two-dimensional infrared (2D-IR) spectra, are presented.

Modern photothermal experiments, including photoacoustic calorimetry (PAC), are capable of measuring molecular volume changes associated with peptide folding and unfolding, isomerizations, and other processes on a picosecond time scale. In this thesis, the application of molecular dynamics techniques to this problem is presented. The method was developed with the hope that it would complement experimental results and provide detailed structural information explaining molecular volume changes. Isobaric-isothermal (NPT) molecular dynamics was used to calculate the volumes of several model systems, including a water molecule, a methane molecule, and a twenty-residue β-sheet peptide, in order to verify the utility of the method and demonstrate the influence of electrostatic interactions on molecular volume. Finally, the molecular volume change
associated with the trans – cis isomerization of azobenzene, a simple organic molecule, was calculated and found to be in excellent agreement with existing experimental results.

Nonlinear spectroscopic techniques provide insight into structure and dynamics that traditional linear methods are unable to probe. While early nonlinear experiments, namely the optical Kerr effect (OKE) and anti-Stokes Raman scattering, did not offer information that linear experiments could not provide, multidimensional techniques, including 2D-Raman and 2D-IR spectroscopy, promised to reveal structural and dynamical details of complicated systems.

In 2D-IR spectroscopy, three time-ordered electrical fields interact with a substance described by its third-order response function \( R^{(3)} \) to generate a third-order polarization \( P^{(3)} \) responsible for the signal. This spectroscopy works on sub-picosecond time scales, allowing it to provide time-resolved structures of transient species, in contrast to established multidimensional NMR and X-ray scattering techniques, which typically yielded time-averaged results. In recent years, 2D-IR spectroscopy has successfully been employed to investigate many intricate problems, including the hydrogen bonding network of water, the three-dimensional structure of peptides, and organic molecules. Since the complicated nature of the resulting spectra often make their interpretation problematic, the application of theoretical methods to 2D-IR spectroscopy to extract meaning from the spectra is called for. Using a time correlation function (TCF) formalism, the third-order response function responsible for 2D-IR signal, initially a complicated quantum-mechanical expression, was derived in terms of a single classical time correlation function, an entity which is easily calculated via classical molecular dynamics (MD) simulations. The resulting theory was used to compute theoretical 2D-IR spectra of two model systems, neat water and 1,3-cyclohexanedione solvated in deuterated chloroform.

In Chapter 2, the molecular dynamics techniques used to calculate molecular volumes are introduced. Chapter 3 outlines the calculation of the molecular volumes of water, the \( \beta \)-sheet peptide, and methane and also describes the role of electrostatic
interactions in these calculations. Chapter 4 includes the results of the experimental and theoretical determination of the volume change associated with azobenzene’s trans – cis isomerization.

The time correlation function formalism, as it arises from Fermi’s Golden rule, is introduced in Chapter 5. Chapters 6 and 7, which contain the developments of TCF theories for the linear response function and the fifth-order response function associated with 2D-Raman experiments, respectively, are provided as background for the two-dimensional infrared spectroscopic theory presented in subsequent chapters.

Chapter 8 introduces the 2DIR experiment and the theory. In this chapter, analytical manipulations are utilized to simplify the third-order response function exactly. Further simplifications, accomplished using harmonic and anharmonic oscillator approximations are discussed in Chapters 9 and 10, respectively. Finally, the computational implementation of the 2D-IR TCF theory is discussed and theoretical spectra of neat water and 1,3-cyclohexanedione are displayed in Chapter 11. Chapter 12 concludes this work and reflects on potential future applications of these theoretical techniques.
Chapter 2

Calculating Molecular Volume: Molecular Dynamics Techniques

Photothermal methods, including photoacoustic calorimetry (PAC) and photothermal beam deflection (PBD), permit the measurement of molecular volume changes of solvated molecules on nanosecond time scales. Photothermal experiments are useful for investigating the thermodynamic profiles associated with interesting phenomena such as the folding of a peptide. Using molecular dynamics (MD) techniques to mimic experimental measurements provides microscopic understanding of the thermodynamic measurements.

To calculate time-dependent thermodynamic volumes, isothermal-isobaric (NPT) molecular dynamics simulations are performed on the system of interest. NPT molecular dynamics allows the volume of the system to fluctuate over time and results in a statistical uncertainty in the average volumes calculated. It was discovered that simulations lasting a few nanoseconds were capable of discerning volume changes of approximately 1.0 mL/mol, a precision comparable to what can be achieved in the laboratory.

In this chapter, the molecular dynamics techniques employed in calculating molecular volumes are introduced. In Chapter 3, the application of molecular dynamics to several simple model system is discussed, and in Chapter 4, it is demonstrated that these theoretical methods and photoacoustic calorimetry predict the same volume change for the trans-cis isomerization of azobenzene.
2.1 Motivation

A productive use of molecular dynamics is to simulate the processes examined in photothermal experiments, which determine molecular volume changes on nanosecond time scales\textsuperscript{1–3} and gain microscopic insight into the experimental results. Such experiments are capable of identifying protein and peptide intermediates with characteristic volumes that have lifetimes of several nanoseconds. Statistically significant changes in the volume coordinate over time indicate the possible presence of transient species, signaled by metastable equilibrium between the solute and solvent. The MD methods employed in this research allow the identification of intermediate structures on the microscopic level. Photothermal experiments also can map out enthalpy profiles over similar time scales, and MD simulations may be used to provide molecular interpretations of these energetics.

2.2 Molecular Dynamics in Calculating Molecular Volume

Classical extended-system isothermal-isobaric (NPT)\textsuperscript{4,5} molecular dynamics simulations play an essential role in computationally determining molecular volume changes. The thermodynamic volume of a system, often consisting of a solute molecule and solvent, can be extracted directly from an NPT MD simulation’s volume coordinate. To obtain the volume of the solute molecule alone, it is straightforward to obtain the volume of the solvent alone and subtract it from the total system volume. One possible method of computing the solvent volume is to ”pluck” the solvated species from the system and re-equilibrate the solvent in the absence of solvent-solute forces. ”Plucking” the molecule from what was an equilibrated system provides an initial condition configurationally near a new equilibrium, and the new equilibrium is quickly achieved. Upon re-equilibration, the volume of the solvent is easily determined from the volume coordinate.
This method is useful for simple solutions, but also may prove helpful in examining complex biological systems composed of intricate assemblies of biomolecules and solvents. While other effective methods of calculating molecular volumes exist, the method proposed is ideal for modeling the time evolution of biological systems. NPT molecular dynamics simulations give rise to a fluctuating volume coordinate. The system’s thermodynamic volume is taken simply as the average volume over the course of the simulation. Upon determining the average volume, it becomes necessary to assess the uncertainty associated with the average. In Section 2.3, it is demonstrated that the volume fluctuations associated with NPT molecular dynamics are Gaussian in nature. Consequently, the standard deviation in volume is a useful measure of the uncertainty.

One important consideration in using NPT molecular dynamics to calculate volume averages is that, as a result of the dynamical nature of MD simulations, successive volume values are not statistically independent. To avoid averaging non-independent volume measurements, it is necessary to calculate the correlation time of the volume coordinate and sample data points which are uncorrelated.

Another concern worth noting is that, although the method employed in our simulations samples the NPT ensemble exactly, NPT MD algorithms are not strictly equivalent to microcanonical dynamics. NPT methods couple real system variables to fictitious variables that regulate thermodynamic properties, e.g. thermostats for temperature and barostats for pressure, in such a way that they fluctuate around pre-determined average values. The methods for calculating thermodynamic volumes are exact for a given potential energy model, but it is uncertain whether dynamical events observed are physically
relevant. NPT dynamics are only slightly perturbed from true Newtonian motion (on the order of $1/\sqrt{3N}$, where $N$ is the number of atoms in the system) relative to microcanonical (NVE) dynamics. Thus, the NPT ensemble is often recommended as one of the more reliable means of simulating biological systems.\textsuperscript{13} If the reliability of isothermal-isobaric dynamics is a concern, the repetition of simulations in the microcanonical ensemble may serve to verify the results.

2.3 Calculating Uncertainty

As stated earlier, fluctuations of observable quantities, such as volume, from their means during the course of an NPT MD simulation, are typically Gaussian and characterized by their standard deviation $\sigma/\sqrt{N}$. Figure 2.1, a histogram of the volumes measured (in mL/mol) during a molecular dynamics simulation of aqueous $cis$-azobenzene, demonstrates the Gaussian nature of volume fluctuations in NPT molecular dynamics.

If successive measurements of molecular volume were uncorrelated, the uncertainty in volume would be simply be calculated as the standard deviation associated with the set of measurements:

$$
\Delta V = \sigma/\sqrt{N} \tag{2.1}
$$

In Equation 2.1, $N$ is the total number of samples. When measurements, such as instantaneous volumes, are closely spaced, they cannot be considered statistically independent. They are inherently connected by the dynamical equations of motion that drive molecular dynamics simulations. To remedy this problem, a correlation time defined
Figure 2.1: A histogram of the volumes (in mL/mol) measured in a molecular dynamics simulation of aqueous cis-azobenzene is displayed. This plot demonstrates the Gaussian nature of volume fluctuations in isothermal-isobaric (NPT) molecular dynamics.
by $t_c = s \delta t$ beyond which measurements are considered independent, is defined. The time step between successive measurements $\delta t$ is multiplied by the statistical inefficiency $s$, which indicates the number of correlated data measurements,\textsuperscript{10,12} to obtain correlation time $t_c$.

The statistical inefficiency is determined by performing volume averages over blocks of time of increasing duration ending with the length of the entire MD run. This parameter $s$ is formally defined by Friedberg and Cameron\textsuperscript{11}:

$$s = \lim_{\tau_B \rightarrow \infty} \frac{\tau_B \sigma^2_B}{\sigma^2}$$

(2.2)

$$\sigma^2_B = \left( \frac{1}{N_B} \right) \sum_{B=1}^{N_B} (\langle V \rangle_B - \langle V \rangle)$$

(2.3)

In Equation 2.2, $N_B$ represents the number of blocks containing $\tau_B$ measurements such that the product $\tau_B N_B = N$, the total number of observations. Based on this information, the correlations between successive volume measurements yields a modified expression for volume uncertainty:

$$\Delta V = \sigma \sqrt{s/N}$$

(2.4)

If the time between measurements exceeds $t_c$, the value of $s$ approaches unity, and Equation 2.4 reduces to Equation 2.1. When performing long MD simulations, it is convenient to space measurements at $\Delta t$ slightly greater than $t_c$ in order to minimize the amount of data stored and to allow the uncertainty to be calculated simply as the
standard deviation. Correlation time $t_c$ for a given system can be determined initially from the results of a preliminary MD simulation.

As the length of a simulation increases, the uncertainty decreases, allowing smaller and smaller molecular volume changes to be resolved. To demonstrate this phenomenon, the uncertainty associated with cis-azobenzene’s volume is considered. Based on a measured correlation time of 1.4 ps, the standard deviation of cis-azobenzene’s volume is computed as a function of increasing simulation time. The result is shown in Figure 2.2. The uncertainty of the volume decreases as the square root of the number of volume measurements. By the time the simulation length reaches 50 ns, a time scale relevant to photothermal experiments, the uncertainty in volume falls to less than 0.5 mL/mol. At this point, it should certainly be possible to recognize relatively modest changes in volume associated with changes in this molecule’s conformation. Examination of the uncertainties in other systems’ volumes yields similar results, indicating that 50 ns of dynamics can generally provide useful information about molecular volumes. For example, a helix-to-coil transition in a peptide is estimated to bring about a volume change of approximately 3.0 mL/mol/residue,$^{14}$ a change which should easily be discerned with 50 ns of dynamics.

All molecular dynamics simulations used in molecular volume calculations were carried out using a code developed by the Klein research group at the Center for Molecular Modeling at the University of Pennsylvania. The code was implemented with parallel execution, extended system particle mesh Ewald summation, and multiple timescale integration algorithms.$^{15,16}$
Figure 2.2: The volume uncertainty of aqueous cis-azobenzene is displayed as a function of simulation length. By 50 ns, a time scale relevant to photothermal experiments, the uncertainty in volume falls to less than 0.5 mL/mol.
Chapter 3

Calculating Molecular Volume: Model Systems

In this chapter, the use of molecular dynamics techniques in the calculation of thermodynamics volumes is demonstrated for several model systems, including a water molecule, a small aqueous peptide, and a methane molecule. The water molecule’s calculated volume is in excellent agreement with accepted values, confirming the model’s ability to capture molecular volumes correctly. The simulation of the peptide, although yielding inconclusive results about the difference in volume between its folded and unfolded states, hints at the potential of the method to discern volume changes in larger proteins. In the analysis of methane, the effect of electrostatics on the molecule’s effective volume is examined by manipulating the atomic charges on the methane molecule. The effect of electrostatics on calculated molecular volume, especially in the case of anionic and cationic methane, is dramatic and conforms to experimentally determined trends. The information obtained from these model systems will aid in setting up and executing the simulation of other systems of interest.
3.1 Volume of a Water Molecule

As an initial test of this approach to measuring molecular volume, the molar volume of neat water, a subject of earlier computational investigations, was determined. The volume of a flexible single point charge water molecule was calculated to high precision at a temperature of 298 K and a pressure of 1.0 atmospheres. The result was 18.0 ± 0.0057 mL/mol, a value which corroborates existing results. This precise value of a water molecule’s volume was used to determine the solvent volumes in several systems investigated using these molecular dynamics methods.

3.2 Volume of a Simple Peptide

Since one potential use of this method is to calculate volume changes associated with the folding of peptides, it was applied to a twenty-residue β-sheet peptide which has recently been under investigation with photothermal methods. The peptide is depicted in Figure 3.1. A “caged” form of the unfolded β-sheet, which can be photolyzed in neat water to initiate folding, was synthesized by Chan and co-workers. Using photothermal methods, it is possible to construct volume and enthalpy profiles associated with the 1.0-μs folding process.

For the purposes of the computational investigation, the initial folded β-sheet peptide was constructed from the NMR structure. The sequence of the protein is given below:
Figure 3.1: An image of the β-sheet peptide is shown in both panels. In the right panel, it is solvated with water, and in the left, it is displayed without solvent for easier visualization. The colors represent atom types: C (green), O (red), N (blue), H (white).

\[ \text{ACE} - \text{VAL} - \text{PHE} - \text{ILE} - \text{THR} - \text{SER} - \text{PRO} - \text{GLY} - \text{LYS} - \text{THR} - \text{TYR} - \text{THR} - \text{GLU} - \text{VAL} - \text{PRO} - \text{GLY} - \text{LYS} - \text{ILE} - \text{LEU} - \text{GLN} \] (3.1)

Additionally, an unfolded configuration of the peptide was built and simulated to provide a basis for comparing the volumes of the folded and unfolded states. Both peptide systems were solvated with 810 flexible SPC water molecules. The AMBER f99 force field\(^{22}\) was used to describe the bonds, bends, torsions, Van der Waals interactions, and non-bonded interactions between atoms separated by three bonds (known as one-four interactions) in the peptide, and the peptide was configured to have no net charge. Figure 3.2 displays the volumes of the solvated folded peptide and the water solvent over
Figure 3.2: The red curve displays the volume fluctuations of the folded aqueous $\beta$-sheet peptide. The blue curve displays the volume fluctuations of the water solvent after the peptide is “plucked” out. The inset demonstrates that the water re-equilibrates and its volume stabilizes quickly, within 0.05 ns, once the peptide is removed.

2.0 ns of simulation time. The inset in Figure 3.2 demonstrates that, after the peptide is “plucked” out of the water solvent, the water re-equilibrates and its volume stabilizes quickly, within 0.05 ns.

7.5 ns of dynamics on the folded $\beta$-sheet gave a volume of $1668.0 \pm 2.4$ mL/mol, while 5.8 ns on the unfolded configuration gave $1672.0 \pm 3.1$ mL/mol. The solution volume of the peptides were computed by subtracting from the total system volume the precise volumes of the water molecules, as determined in Section 3.1. It is somewhat surprising that the folded and unfolded states, within the uncertainties stated,
have essentially the same volume since the solvation structures associated with each are markedly different. This surprising result does not necessarily suggest that dynamical intermediates with significantly different volumes are not present during the folding process. However, longer simulations of both states should be attempted before drawing any firm conclusions about the volume change associated with the $\beta$-sheet’s folding process.

Although the investigation of the small $\beta$-sheet was inconclusive, larger proteins, which often exhibit larger per-residue volume changes during folding, may be ideal subjects for this method of calculating molecular volume changes.

### 3.3 Volume of a Methane Molecule and Electrostatic Effects

As a final test of the method, the volume of a single methane molecule solvated by 62 water molecules was measured at ambient conditions (temperature of 298 K and pressure of 1.0 atmospheres). An all-atom methane motel, including a flexible force-field fit, was used to reproduce experimental infrared frequencies with harmonic carbon-hydrogen bonds.$^{23}$ Lennard-Jones interactions were applied only between the methane carbon and water oxygens with parameters $\sigma = 3.33$ Angstroms and $\epsilon = 51.0$ K. The equilibrium carbon-hydrogen bond length was set at 1.09 Angstroms, and the molecule was assumed to have tetrahedral geometry. To measure the effects of electrostatic forces in solvation, aqueous methane was simulated using a variety of models, each placing different partial charges on methane’s carbon and hydrogen atoms.

The partial charges in the first model of $-0.52 \, e^-$ on carbon and $+0.13 \, e^-$ on each of the hydrogen atoms were fit to the electrostatic potential surface calculated
using *ab initio* electronic structure methods that reproduce the octupole moment of gas phase methane. Applying these realistic partial charges resulted in a calculated volume of $31.54 \pm 0.41 \text{mL/mol}$. In contrast, a methane molecule with all partial charges removed exhibited a volume of $31.74 \pm 0.41 \text{mL/mol}$. Both results were obtained from 10.0 ns of dynamics. The volume difference between the two versions of methane is statistically insignificant. This result is not surprising, given that the electrostriction effects associated with the highly symmetric methane molecule, which lacks a permanent dipole, quadrupole, and octupole moment, are considered negligible.

To more closely examine the effects of electrostatic moments on solvation and the solution volume of the methane molecule dipolar methane, which does not represent a realistic methane molecule, was simulated. The dipolar methane was constructed by placing a partial charge of $+0.52 \, e^-$ on the carbon atom and $-0.52 \, e^-$ on one of the hydrogen atoms. The other three atoms were taken as uncharged. The resulting dipole moment on the methane molecule was 2.7 Debye, slightly larger than water’s dipole moment of 2.4 Debye. In comparison to the uncharged methane molecule described earlier in this section, the dipolar methane exhibited a volume constriction of $1.73 \pm 1.02 \text{mL/mol}$. This relatively small volume change is consistent with the negligible volume change occurring when octupolar methane is solvated in water.

While dipolar and octupolar methane do not exhibit significant volume decreases due to electrostriction, the simulation of monopolar (charged) methane molecules yielded striking results. The methane anion and cation are constructed by placing charges of $+e^-$ and $-e^-$, respectively, on the carbon atom. The four hydrogen atoms are left uncharged.
These snapshots depict the solvated methane cation (left panel) and anion (right panel). The ordering of water molecules around the carbon (the green atom) of methane is apparent in each snapshot.

Compared to the uncharged methane molecule, the cation exhibited a volume change of $-20.96 \pm 0.39$ mL/mol, based on 10.0 ns of dynamics. The anion experienced an even more dramatic change of $-40.13 \pm 0.48$ mL/mol, based on 12.0 ns of dynamics, a volume change which gives the molecule a negative volume when solvated. Both results demonstrate the significant effect that electrostatics can have on calculated molecular volumes and highlight the importance of carefully accounting for electrostatic interactions in any simulation.

The difference seen in the volumes of the anion and cation can be attributed to the nature of the methane molecule’s solvation. Figure 3.3 depicts the solvated anionic and cationic methane molecules. In the first panel, which displays the solvated cationic methane, the water’s electronegative oxygen atoms are aligned to be as close to the positively charged carbon atom. In the second panel, which shows the solvation of the anion,
Figure 3.4: The radial distribution function between the methane carbon and water hydrogen atoms. The solid red line represents anionic methane, the dashed green line cationic methane, and the dotted blue line neutral methane. The carbon-hydrogen first neighbor peak of the anionic methane is sharply shifted to the left relative to the other two forms of methane, indicating that the hydrogens penetrate the van der Waals sphere of anionic methane’s carbon.

The water molecules align themselves with hydrogens pointing towards the negatively charged carbon atom. Because the hydrogens are less bulky than the oxygen atom in water, the water molecules effectively move closer to the methane anion than to the cation, allowing for greater electrostriction of the solvent.

Examination of the radial distribution functions between the methane carbon and water hydrogen (Figure 3.4) and oxygen (Figure 3.5) atoms confirms the arrangements
Figure 3.5: The radial distribution function between the methane carbon and water oxygen atoms. The solid red line represents anionic methane, the dashed green line cationic methane, and the dotted blue line neutral methane. The sharp first neighbor peaks for cationic and anionic methane suggest that the solvent is more highly ordered around the methane carbon than it is for the neutral form of methane.
of atoms suggested in the simulation snapshots. The anionic methane allows water’s hydrogen atoms to penetrate into the carbon atom’s van der Waals sphere at a distance of 1.5-2.2 Angstroms. Thus, as clearly displayed in its carbon-hydrogen first neighbor peak, which is shifted dramatically to the left of the neutral form’s, anionic methane is much more tightly solvated than neutral methane, indicated by the blue dotted lines. The close coordination of the carbon and hydrogen atoms in anionic methane’s solvation maximizes the interaction between the negatively charged carbon atom and partially positively charged hydrogen atoms. Cationic methane, indicated by green dashed lines, is more tightly solvated than the neutral form, as demonstrated by its carbon-oxygen first neighbor peak. Both anionic and cationic methane possess a sharp carbon-hydrogen first neighbor peak, which suggest the presence of a structured solvation shell.

The simulation snapshots and radial distribution functions of anionic, cationic, and neutral methane demonstrate that molecular dynamics can provide an effective microscopic picture of the electrostatic interactions that drive molecular volume changes. The conclusion that anionic solvation yields larger volume contractions than cationic solvation is consistent with experimentally measured trends.\textsuperscript{25}

The application of this molecular dynamics method to the model systems of water, the $\beta$-sheet, and methane demonstrate its powerful ability to assess molecular volume changes associated with solvation under varying electrostatic conditions. In Chapter 4, the method will be used to assess the volume change associated with azobenzene’s \textit{trans-cis} isomerization, a volume change which has been measured experimentally using photoacoustic calorimetry.\textsuperscript{26}
Chapter 4

Calculating Molecular Volume: Azobenzene’s Isomerization

In this chapter, the molecular dynamics method for determining molecular volume changes, outlined in Chapter 2 and applied to several model systems in Chapter 3, is used to measure the molecular volume change associated with the trans-cis isomerization of the simple organic molecule azobenzene. The results of the simulation are found to be in excellent agreement with the experimental volume change, measured by Professor Randy Larsen’s laboratory at the University of South Florida, determined using photoacoustic calorimetry (PAC).

4.1 Azobenzene Experimental Details

In the PAC experiment, laser pulses are used to photoisomerize a sample of aqueous trans azobenzene to the cis form. Excess energy not used in the isomerization process generates an acoustic wave, which is detected by a microphone and measured with an oscilloscope. The amplitude of the acoustic signal is proportional to the molecular volume change associated with azobenzene’s isomerization.

To isolate the trans isomer of azobenzene, 5 mg of solid azobenzene was dissolved in 2 mL of absolute ethanol. The solution was illuminated with a halogen lamp and
diluted with five volumes of deionized water. The *trans* isomer, which is only sparingly soluble in water, was then filtered out. The sample to be used in the PAC measurements was prepared by saturating a water solution with the solid *trans* azobenzene.

In the absence of light, both the *cis* and *trans* isomers of azobenzene can remain as metastable aqueous isomers for several hours. Upon illumination, a rapid photoisomerization occurs, and a molecular volume change, which is measured by PAC, accompanies the conformational transition.

The sample and calorimetric reference acoustic traces were obtained as functions of temperature, and the ratio of the amplitudes of the acoustic signals $S/R$ was plotted versus $1/(\beta/C_p\rho)$.

$$\frac{S}{R}E_{hv} = \phi E_{hv} = \Phi [Q + (\Delta V_{con}/(\beta/C_p\rho))] \tag{4.1}$$

In Equation 4.1, $\Phi$ is the quantum yield, which took on a value of 0.26 in this experiment. $Q$ is the heat released to the solvent, $\beta$ is the coefficient of thermal expansion of the solvent (K$^{-1}$), $C_p$ is the heat capacity (cal g$^{-1}$ K$^{-1}$), $\rho$ is the density (g/mL), and $\Delta V_{con}$ denotes the conformational and electrostriction contributions to the solution volume change of the azobenzene molecule. A plot of $\phi E_{hv}$ is expected to give a straight line with a slope of $\Phi \Delta V_{con}$. Subtracting $\Phi Q$ from $E_{hv}$ also yields the enthalpy change $\delta H$ associated with processes faster than the time scale of the instrument, approximately 50 ns.

A plot of the experimental data revealed that photoisomerization of *trans*-azobenzene to the *cis* form yielded a volume change of $-4 \pm 1$ mL/mol. The observed volume con-
traction was similar to that observed in 80:20 ethanol:water, as well as the volume change associated with aqueous carboxyl-azobenzene.\textsuperscript{26}

### 4.2 Azobenzene Simulation Details

Initial structures for \textit{cis} and \textit{trans} azobenzene were built and optimized using the GAMESS package\textsuperscript{27} and a 6-31G* basis set. The resulting structures were compared with established crystal structures and were determined to be superimposable and virtually indistinguishable. The Amber f99\textsuperscript{22} force field provided bond, bend, torsion, one-four, and van der Waals interaction parameters, and the partial charges on azobenzene’s atoms were fit to the electrostatic potential surface using the Connolly method in the GAMESS package.\textsuperscript{27} Azobenzene’s \textit{trans} isomer is a planar molecule which has a net dipole of zero due to its symmetry, while the \textit{cis} isomer is a nonplanar structure with a large gas phase dipole of 3.45 Debye. All simulations included 108 explicit flexible SPC water molecules. Figure 4.1 depicts the gas-phase and solvated \textit{cis} and \textit{trans} azobenzene molecules.

The zero volume reference was provided by an NPT simulation of a box of 108 flexible SPC water molecules. The difference between a solvated azobenzene isomer and the volume of the neat water was taken as the molecular volume of each isomer. The difference between the molecular volumes of the \textit{trans} and \textit{cis} azobenzene isomers was taken as the molecular volume associated with azobenzene’s \textit{trans} – \textit{cis} isomerization.

The correlation time associated with azobenzene’s volume was determined to be 1.4 ps. Based on this information, volume measurements were recorded every 2.0 ps to ensure that successive measurements were statistically independent. The uncertainty in
Figure 4.1: Equilibrium solvated structures of cis (left) and trans (right) azobenzene are depicted. The top panels show the gas-phase structures, and the bottom panels show the molecules solvated with 108 water molecules. The molecule types are represented as follows: red (O), white (H), green (C), blue (N).
Figure 4.2: Volume fluctuations for both cis (red) and trans (green) azobenzene, as well as neat water (blue) during 100 ns of dynamics are displayed. The average values of the volumes are represented as straight dashed lines.

Each isomer’s molecular volume was taken as the standard deviation associated with each set of measurements.

4.3 Computational Results and Discussion

Traces of the solvated azobenzene volume fluctuations for 100 ps of dynamics are displayed in Figure 4.2. The top two traces represent the volumes of cis and trans azobenzene, while the bottom trace represents the solvent volume.

The results of azobenzene’s simulation are summarized in Table 4.3. Based on 72 ns of dynamics, the volumes of cis and trans-azobenzene were determined to be 148.2
Table 4.1: *This table displays the molecular volumes calculated for cis and trans azobenzene, both the charged and uncharged systems. In the final column, the volume change associated with the trans-cis isomerization is shown. All results are given in mL/mol.*

<table>
<thead>
<tr>
<th>System</th>
<th>cis</th>
<th>trans</th>
<th>ΔV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charged</td>
<td>148.2 ± 0.3</td>
<td>151.8 ± 0.3</td>
<td>-3.56 ± 0.6</td>
</tr>
<tr>
<td>Uncharged</td>
<td>152.6 ± 0.4</td>
<td>148.8 ± 0.4</td>
<td>3.8 ± 0.8</td>
</tr>
</tbody>
</table>

± 0.3 mL/mol and 151.8 ± 0.3 mL/mol, respectively. The volume change associated with isomerization is -3.56 ± 0.6 mL/mol, a result which compares favorably with the experimental molecular volume change. The absolute volumes also conform closely to the volumes of the crystal structures: 149-150 mL/mol for cis-azobenzene and 148-149 mL/mol for trans-azobenzene. While these numbers are not strictly comparable due to the different chemical environments associated with aqueous and crystalline azobenzene, the agreement is striking.

Examination of the radial distribution function of azobenzene’s nitrogen atoms with the water hydrogen atoms, displayed in Figure 4.3, confirms these results. The radial distribution function associated with cis-azobenzene exhibits a marked first neighbor peak shifted slightly to the left of trans-azobenzene’s broad first neighbor peak. This peak suggests ordering of the solvent and closer proximity of water’s hydrogen atoms to cis-azobenzene’s nitrogen atoms. The tighter solvation of cis-azobenzene, relative to the trans form, results in a reduced molecular volume.
Figure 4.3: The radial distribution function of azobenzene’s nitrogen atoms with water’s hydrogen atoms is displayed. The blue line indicates cis-azobenzene, and the red line trans-azobenzene. The marked first neighbor peak for the cis form indicates ordering of the solvent and closer proximity of the solvent molecules to cis-azobenzene’s nitrogen atoms.
Molecular volumes are often considered in terms of Van der Waals radii and the manner in which the overlapping spheres fill space. While steric interactions play a major role in determining molecular volumes, as demonstrated in Chapter 3, electrostatic interactions also must be examined, especially in measuring dynamical volume changes.

To assess the role of electrostriction in azobenzene’s volume change, both aqueous azobenzene molecules were simulated with the atomic charges removed. In this case, the volumes of cis and trans-azobenzene were determined to be 152.6 ± 0.4 mL/mol and 148.8 ± 0.4 mL/mol, respectively, based on 40.5 ns of dynamics. The volume of the cis isomer is now significantly larger than the trans, a result consistent with its larger crystal structure and bulkier three-dimensional structure. This result also suggests that cis-azobenzene’s large dipole is responsible for an excess electrostriction of 8 mL/mol, which makes the sterically larger cis isomer have a smaller solvated volume than the trans isomer.

This study of azobenzene demonstrates the ability of this combined theoretical and experimental approach to provide atomistic resolution of the origin of molecular volume changes. While the method is applied to a volume change between two equilibrium states in this case, it may also be used to accurately describe the changes in shape and volume associated with intermediates along a reaction pathway.
Chapter 5

Time Correlation Function Formalism

Time correlation function (TCF) theories are useful for linking the nature of a system’s dynamics to spectra generated using innovative experimental techniques, such as sum frequency generation, two-dimensional Raman, and two-dimensional infrared spectroscopy. In this chapter, the time correlation function formalism’s natural connection to Fermi’s Golden Rule and time-dependent perturbation theory is outlined. In Chapters 6 and 7, the derivations of TCF theories for one-dimensional nonlinear spectroscopy and the fifth-order response function $R^{(5)}$ are discussed as background for the development of a TCF theory of two-dimensional infrared spectroscopy, described in Chapters 8-10.

5.1 Linear Absorption of Radiation

This analysis begins with a system of $N$ interacting molecules in initial quantum state $i$. The system is described by its Hamiltonian $H_0$, where $H_0 \psi_j = E_j \psi_j$. The system interacts with a monochromatic electric field of frequency $\omega$, described by Equation 5.1.

$$E(t) = E_0 \epsilon \cos(\omega t) = E_0 \epsilon (e^{i\omega t} + e^{-i\omega t})$$

(5.1)
$E_0$ is the amplitude of the field and $\epsilon$ is a unit vector indicating the direction of the field. The field is considered to be spatially uniform and the wavelength significantly greater than the size of the interacting molecules. Using these assumptions, the interaction between the field and the molecules, which acts as a perturbation to $H_0$, is written as shown.

$$H^{(1)}(t) = -M \cdot E(t)$$  \hspace{1cm} (5.2)

$M$ is the total electric dipole moment operator of the system. According to the Fermi Golden rule of time-dependent perturbation theory, the probability per unit time that a transition from initial state $i$ to final state $f$ will occur is given by Equation 5.3.

$$P_{i \rightarrow f}(\omega) = \frac{\pi E_0^2}{2\hbar^2} |\langle f | \epsilon \cdot M | i \rangle|^2 [\delta(\omega_{fi} - \omega) + \delta(\omega_{fi} + \omega)]$$  \hspace{1cm} (5.3)

Multiplying Equation 5.3 by $\hbar \omega_{fi}$, the energy difference between the final and initial states, gives the rate of energy lost from the radiation in the transition from state $i$ to $f$. Summing over all states $f$ yields the energy lost in transitioning from state $i$ to any other state. Finally, multiplying by the probability $\rho_i$ of being in state $i$ and summing over all $i$ gives $\dot{E}_{rad}$, the rate of energy loss from the radiation to the system during the transition.
\[ -\dot{E}_{\text{rad}} = \sum_i \sum_f \rho_i \hbar \omega_{fi} P_{i \rightarrow f} \]

\[ -\dot{E}_{\text{rad}} = \frac{\pi E_0^2}{2\hbar} \sum_f \sum_i \omega_{fi} \rho_i |\langle f |\varepsilon \cdot M |i \rangle|^2 [\delta(\omega_{fi} - \omega) + \delta(\omega_{fi} + \omega)] \]  

(5.4)

It is reasonable to switch the \( i \) and \( f \) indices in the sum over the second delta function, since \( i \) and \( f \) incorporate all quantum states of the system. This allows the simplification of Equation 5.4.

\[ -\dot{E}_{\text{rad}} = \frac{\pi E_0^2}{2\hbar} \sum_f \sum_i \omega_{fi} (\rho_i - \rho_f) |\langle f |\varepsilon \cdot M |i \rangle|^2 \delta(\omega_{fi} - \omega) \]  

(5.5)

If the system is initially in equilibrium, \( \rho_f = e^{-\beta \hbar \omega_f} \rho_i \). Also, enforcing the delta function in Equation 5.5 allows all \( \omega_{fi} \) to be written simply as \( \omega \) and pulled out of the sum.

\[ -\dot{E}_{\text{rad}} = \frac{\pi E_0^2}{2\hbar} \omega (1 - e^{-\beta \hbar \omega}) \sum_f \sum_i \rho_i |\langle f |\varepsilon \cdot M |i \rangle|^2 \delta(\omega_{fi} - \omega) \]  

(5.6)

The absorptive cross-section \( \alpha(\omega) \) is defined as the ratio of the radiation loss \( \dot{E}_{\text{rad}} \) to the incident flux of radiation \( S \), shown below in Equation 5.7.

\[ S = \frac{c}{8\pi n E_0^2} \]  

(5.7)

\( c \) represents the speed of light in a vacuum and \( n \) is the index of refraction of the medium. Using Equations 5.6 and 5.7, the absorptive cross-section can be derived.
\[ \alpha(\omega) = \frac{\dot{E}_{\text{rad}}}{S} \frac{4\pi^2}{\hbar c n} \omega (1 - e^{-\beta n \omega}) \sum_f \sum_i \rho_i |\langle f|\varepsilon \cdot M|i\rangle|^2 \delta(\omega_f - \omega) \] (5.8)

Equation 5.8 may be used to define an absorption lineshape \( I(\omega) \), which is defined below in Equation 5.9.

\[ I(\omega) = \frac{3\hbar c n \alpha(\omega)}{4\pi^2 \omega (1 - e^{-\beta n \omega})} \]

\[ I(\omega) = 3 \sum_i \sum_f \rho_i |\langle f|\varepsilon \cdot M|i\rangle|^2 \delta(\omega_f - \omega) \] (5.9)

To derive a time correlation function of spectroscopy, Equation 5.9 should be written in the Heisenberg representation. This is accomplished by introducing the Dirac delta function, defined below.

\[ \delta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} dt \] (5.10)

Incorporating the Dirac delta function into the lineshape expression gives Equation 5.11.

\[ I(\omega) = \frac{3}{2\pi} \sum_i \sum_f \rho_i |\langle i|\varepsilon \cdot M|f\rangle| \langle f|\varepsilon \cdot M|i\rangle \int_{-\infty}^{\infty} e^{[E_f - E_i]/\hbar - \omega]t} dt \] (5.11)
States $i$ and $j$ are eigenstates of the unperturbed system, implying that $e^{-iE_i t/\hbar}|i\rangle - e^{-iE_j t/\hbar}|j\rangle$ and $\langle f|e^{-iE_j t/\hbar} = \langle f|e^{iH_0 t}/\hbar$. Using this information, Equation 5.11 can be simplified even further.

$$I(\omega) = \frac{3}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_i M(t) = e^{iH_0 t/\hbar}Me^{-iH_0 t/\hbar}$$

(5.12)

The closure relationship, $\sum_f |f\rangle\langle f|$, allows for the removal of the sum over $f$ from the equation. The sum over initial states $i$ gives an equilibrium ensemble average, which can be represented using angle brackets. Finally, for isotropic fluids, averaging $\epsilon$ over all directions gives the simplified equation shown below in Equation 5.13.

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \langle M(0) \cdot M(t) \rangle dt$$

(5.13)

The lineshape function $I(\omega)$ has now been written as the time correlation function of the absorbing molecules’ dipole moment operator in the absence of the electric field perturbation. Equation 5.13 allows a connection to be formed between an observable, given by $I(\omega)$ and the motions of the molecules’ dipole moments over time.
Chapter 6

TCF Theory: One-Time Correlation Function

The time correlation function theory, besides being relevant to linear spectroscopy, has been applied successfully to nonlinear spectroscopies. It has also been used to demonstrate the lack of new information provided by early nonlinear experiments, such as OKE spectroscopy.\textsuperscript{31–34}

To provide an introduction to the techniques used in the development of the two-dimensional infrared spectroscopy TCF theory, outlines of lower-order theories are provided. In this chapter, the development of the theory of the one-time correlation function associated with OKE and Raman experiments is discussed. Some of the basic procedures used, including the derivation of frequency-domain detailed-balance relationships to simplify response functions, will appear in later chapters.

6.1 The One-Time Correlation Function

This development begins with the third-order response function probed in the third-order Raman experiment.\textsuperscript{34}
\[ R^{(3)}(t) = \frac{i}{\hbar} \langle [\pi(t), \pi(0)] \rangle \] (6.1)

The square brackets denote the commutator of \( \pi(t) \) and \( \pi(0) \), and the angle brackets indicate the quantum mechanical trace. The \( \pi \) is the polarizability of the system. Expansion of the commutator brackets gives

\[ R^{(3)}(t) = \frac{i}{\hbar} \left[ \langle \pi(t)\pi(0) \rangle - \langle \pi(0)\pi(t) \rangle \right] \] (6.2)

The response function is now displayed in terms of two one-time quantum mechanical time correlation functions. Classically, the operators \( \pi(t) \) and \( \pi(0) \) commute suggesting that, in this limit, there is no third-order Raman signal. To develop a means of calculating \( R^{(3)} \) using classical molecular dynamics techniques, it is necessary to rewrite Equation 6.2 in terms of a classical time correlation function, but in such a way that the signal is nonzero.

This is accomplished by deriving Equation 6.2 in terms of the real part of a single quantum mechanical TCF, which is essentially equivalent to a classical time correlation function.

Equation 6.2 actually is the difference between one quantum mechanical TCF \( C(t) \) and its complex conjugate \( C^*(t) \). To prove this, the quantum mechanical traces are taken and the operators are written in the Heisenberg notation, where \( \pi(t) = e^{-iHt/\hbar} \pi e^{-iHt/\hbar} \).
\[ C(t) = \langle \pi(t)\pi(0) \rangle = \frac{1}{\mathcal{Q}} \sum_{a} \langle a | e^{-\beta H} e^{iHt/\hbar} e^{-iHt/\hbar} \pi | a \rangle \]

\[ C^*(t) = \langle \pi(0)\pi(t) \rangle = \frac{1}{\mathcal{Q}} \sum_{a} \langle a | e^{-\beta H} e^{-iHt/\hbar} e^{iHt/\hbar} \pi | a \rangle \]  

(6.3)

Then a complete set of states \( \sum_{b} | b \rangle \langle b | \) is inserted to give the TCFs in another form. Below in Equation 6.4 it is clear that \( \langle \pi(t)\pi(0) \rangle \) and \( \langle \pi(0)\pi(t) \rangle \) are complex conjugates.

\[ C(t) = \frac{1}{\mathcal{Q}} \sum_{a} \sum_{b} e^{-\beta E_a} \pi_{ab} \pi_{ba} e^{iE_{ab}t/\hbar} \]

\[ C^*(t) = \frac{1}{\mathcal{Q}} \sum_{a} \sum_{b} e^{-\beta E_a} \pi_{ab} \pi_{ba} e^{iE_{ba}t/\hbar} \]  

(6.4)

In Equation 6.4 the notation \( E_{ij} \) indicates the energy difference \( E_i - E_j \) and \( \pi_{ij} \) a matrix element \( \langle i | \pi | j \rangle \). Now, the third-order response function is written again in terms of \( C(t) \) and \( C^*(t) \).

\[ R^{(3)}(t) = \frac{i}{\hbar} [C(t) - C^*(t)] \]  

(6.5)

Since \( C(t) = C_R(t) + iC_I(t) \) and \( C^*(t) = C_R(t) - iC_I(t) \), where \( C_R(t) \) is the real part of \( C(t) \) and \( C_I(t) \) is the imaginary part, Equation 6.5 can clearly be written in terms of \( C_I(t) \) only.

\[ R^{(3)}(t) = -\frac{2}{\hbar} C_I(t) \]  

(6.6)

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6.2 Obtaining $R^{(3)}$ in Terms of $C(t)$

Unfortunately, $C_1(t)$ has no classical limit and cannot be calculated via classical techniques. However, it is possible to identify an analytical relationship between the real and imaginary parts of $C(t)$, allowing $R^{(3)}$ to be written as a function of a real TCF which has a valid classical limit. To derive such a relationship, it is helpful to Fourier transform $C(t)$ and $C^*(t)$ to obtain them in the frequency domain.

\[ C(\omega) = FT[C(t)] = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} C(t) dt \] \hspace{1cm} (6.7)
\[ C(-\omega) = FT[C^*(t)] = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} C^*(t) \] \hspace{1cm} (6.8)

The frequency-domain TCFs are shown below. The exponentials appearing in the time-domain TCFs of Equation 6.4 are replaced by delta functions.

\[ C(\omega) = \frac{1}{Q} \sum_a \sum_b e^{-\beta E_a} \pi_{ab} \pi_{ba} \delta(\omega - E_{ab}/\hbar) \] 
\[ C(-\omega) = \frac{1}{Q} \sum_a \sum_b e^{-\beta E_a} \pi_{ab} \pi_{ba} \delta(\omega - E_{ba}/\hbar) \] \hspace{1cm} (6.9)

To relate the two TCFs, it is useful to rewrite $C(-\omega)$ by flipping the indices $a$ and $b$. This action is equivalent to taking a cyclic permutation of the trace.

\[ C(-\omega) = \frac{1}{Q} \sum_a \sum_b e^{-\beta E_b} \pi_{ab} \pi_{ba} \delta(\omega - E_{ab}/\hbar) \] \hspace{1cm} (6.10)
The only difference between $C(\omega)$ and $C(-\omega)$ is now the Boltzmann factor, the first item inside the sum. This implies that

$$C(\omega) = e^{-\beta E_a} e^{\beta E_b} C(-\omega) = e^{\beta E_{ba}} C(-\omega) \quad (6.11)$$

The delta function in Equation 6.10 requires $\omega = E_{ab}$, therefore Equation 6.11 becomes

$$C(\omega) = e^{-\beta \hbar \omega} C(-\omega) \quad (6.12)$$

This detailed-balance relationship between $C(\omega)$ and $C(-\omega)$ may be applied to the frequency-domain response function to simplify it.

$$R^{(3)}(\omega) = \frac{i}{\hbar} [C(\omega) - C(-\omega)] = \frac{i}{\hbar} (1 - e^{\beta \hbar \omega}) C(\omega) \quad (6.13)$$

In the classical limit, the exponential can be expanded out to first order to give the following result.

$$R^{(3)}(\omega) = \frac{i}{\hbar} (\beta \hbar \omega) C(\omega) = i \beta \omega C(\omega) \quad (6.14)$$
6.3 Relating the Real and Imaginary Parts of $C(\omega)$

An alternative means of deriving Equation 6.14 is to derive an analytical relationship between the real and imaginary parts of the frequency-domain TCF $C(\omega)$. This technique, while seemingly redundant in the case of the one-time correlation function, will prove extremely useful in the analysis of higher-order TCFs.

In the time domain, the TCF $C(t)$ is the sum of its real and imaginary parts.

$$C(t) = C_R(t) + iC_I(t) \quad (6.15)$$

The two parts are Fourier transformed separately to obtain $C_R(\omega)$ and $C_I(\omega)$, both of which are real.

$$C_R(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} C_R(t) dt$$
$$C_I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} iC_I(t) dt \quad (6.16)$$

It is easy to define $C_R(\omega)$ and $C_I(\omega)$ in terms of $C(\omega)$ and $C(-\omega)$, given that $FT[C(t)] = C(\omega)$ and $FT[C^*(t)] = C(-\omega)$.

$$C_R(\omega) = \frac{[C(\omega) + C(-\omega)]}{2}$$
$$C_I(\omega) = \frac{[C(\omega) - C(-\omega)]}{2} \quad (6.17)$$

Using the simple detailed-balance relationship defined in Equation 6.12, a ratio between $C_I(\omega)$ and $C_R(\omega)$ is written.
\[ C_I(\omega) = \frac{[1 - e^{-\beta \hbar \omega}]C(\omega)}{[1 + e^{-\beta \hbar \omega}]C(\omega)} C_R(\omega) \quad (6.18) \]

Multiplication of the right-hand side of Equation 6.18 by \(e^{\beta \hbar \omega/2}/e^{-\beta \hbar \omega/2}\) results in a tanh relationship between \(C_I(\omega)\) and \(C_R(\omega)\).

\[ C_I(\omega) = \tanh(\beta \hbar \omega/2)C_R(\omega) \quad (6.19) \]

In the frequency domain, the linear response function is written as the difference of \(C(\omega)\) and \(C(-\omega)\), which is just twice \(C_I(\omega)\).

\[ R^{(3)}(\omega) = \frac{i}{\hbar} [C(\omega) - C(-\omega)] = \frac{i}{\hbar} [2C_I(\omega)] \quad (6.20) \]

Using the newly derived tanh relationship, the result obtained, when the classical limit is taken, is the same as Equation 6.14.

\[ R^{(3)}(\omega) = \frac{i}{\hbar} [2 \tanh(\beta \hbar \omega_2)C_R(\omega)] \]

\[ R^{(3)}(\omega)_{\hbar \to 0} = i \beta \omega C_R(\omega) \quad (6.21) \]
6.4 Transforming to the Time Domain

Since calculations will be performed in the time domain, it is useful to obtain this response function in the time domain. It is easily proven that Equation 6.14 actually represents a time derivative of \( C(t) \).

\[
\frac{dC(t)}{dt} = \frac{d}{dt} \int_{-\infty}^{\infty} e^{i\omega t} C(\omega) d\omega
\]  
\[ (6.22) \]

In Equation 6.22, the right-hand side displays the time derivative of the reverse Fourier transform of \( C(\omega) \), which gives \( C(t) \). Carrying out this derivative yields

\[
\frac{dC(t)}{dt} = i \int_{-\infty}^{\infty} \omega e^{i\omega t} C(\omega) d\omega
\]  
\[ (6.23) \]

In Equation 6.23, the right-hand side represents the reverse Fourier transform of \( \omega C(\omega) \), which appears in the response function. Thus, in the time domain, the response function can be written as a time derivative as shown.

\[
R^{(3)}(t) = \beta \frac{d}{dt} \langle \pi(t) \pi(0) \rangle
\]  
\[ (6.24) \]

Equation 6.24 is written in terms of \( C(t) \), the same TCF that is associated with the linear experiment, as shown in Equation 5.13. This result supports the idea that the nonlinear Raman experiment provides no new information beyond what the linear experiment does.
Chapter 7

TCF Theory: Fifth-Order Raman Spectroscopy

In this chapter, the development of the time correlation function theory of fifth-order Raman spectroscopy is presented. While little attention will be given to the experimental details or computational results, the procedure used in deriving the theory will be discussed thoroughly as a means of providing an introduction to several techniques used in developing the theory of two-dimensional infrared spectroscopy.

Many of the procedures used to derive the fifth-order Raman TCF theory are similar in nature to the techniques used in Chapter 6 to examine the one-time TCFs associated with $R^{(3)}$. Exact frequency-domain detailed-balance relationships are employed to write $R^{(5)}$ in terms of the real and imaginary part of a single quantum mechanical TCF. However, unlike the one-time case, it is not possible to construct an exact $R^{(5)}$ expression that can be calculated in terms of classical TCFs. Therefore, the harmonic oscillator with nonlinear polarizability, the lowest order reference system that gives a signal, is introduced as a means of approximately eliminating the imaginary part of the remaining TCF, thereby making the fifth-order response function's calculation amenable to classical molecular dynamics methods.
7.1 The Fifth-Order Response Function

In the fifth-order Raman experiment, a six wave mixing technique, a pair of fs pulses at time zero excite a system, leaving it in a vibrational coherence. After a time delay $t_1$, during which the system undergoes free evolution, the system is excited by a second pair of pulses that transfers it to a new vibrational coherence or population state. After another time delay $t_2$, a single pulse probes the system. The observable of interest in the fifth-order Raman experiment is the fifth-order polarization $P^{(5)}(t)$, which is represented as the convolution of the incident electric fields with the fifth-order response function $R^{(5)}(t_1, t_2)$. The quantum mechanical expression for the electronically nonresonant fifth order polarization response is given by $^{34,39-41}$

$$R^{(5)}(t_1, t_2) = - \left( \frac{1}{\hbar^2} \right) Tr\{\Pi^{\alpha\beta}(t_1 + t_2)[\Pi^{\gamma\delta}(t_1), [\Pi^{\epsilon\phi}(0), \rho]]\} \quad (7.1)$$

In Equation 7.1, $\rho = e^{-\beta H}/Q$ for a system described by Hamiltonian $H$ and partition function $Q$. The variable $\beta$ represents the reciprocal temperature $1/kT$, where $k$ is Boltzmann’s constant. $\Pi$ represents the system’s polarizability tensor and the Greek superscripts are the elements under consideration.

Expansion of the commutators reveals that $R^{(5)}$ appears in terms of two quantum mechanical TCFs, defined as $f(t_1, t_2)$ and $g(t_1, t_2)$, and their complex conjugates $f^*(t_1, t_2)$ and $g^*(t_1, t_2)$. The response function itself is real in time, while the individual TCFs are complex.
\[ R^{(5)}(t_1, t_2) = -\left( \frac{1}{\hbar^2} \right) [g(t_1, t_2) - f^*(t_1, t_2) - f(t_1, t_2) + g^*(t_1, t_2)] \] (7.2)

The two TCFs and their complex conjugates are defined by

\[ f(t_1, t_2) = \langle \Pi^*(t_1)\Pi(t_2)\Pi(0) \rangle \]
\[ f^*(t_1, t_2) = \langle \Pi(0)\Pi(t_2)\Pi^*(t_1) \rangle \]

\[ g(t_1, t_2) = \langle \Pi(t_2)\Pi(0)\Pi^*(t_1) \rangle \]
\[ g^*(t_1, t_2) = \langle \Pi^*(t_1)\Pi(0)\Pi(t_2) \rangle \] (7.3)

Notice that in the classical limit, the \( \Pi \) operators commute, making TCFs \( f \) and \( g \) equivalent, and the entire \( R^{(5)} \) expression, as written, becomes zero. In Equation 7.2, the contents of the square brackets represent the difference between the real parts of TCFs \( g(t_1, t_2) \) and \( f(t_1, t_2) \), i.e. \( g_R(t_1, t_2) - f_R(t_1, t_2) \).

In the classical limit, the trace in Equation 7.1 must have a leading \( \hbar^2 \) prefactor to cancel the \( 1/\hbar^2 \) shown in the equation. Using exact frequency-domain detailed-balance relationships between the two quantum mechanical TCFs, it will be possible to extract one of these \( \hbar \). After this step, the expression remains in terms of the real and imaginary parts of one TCF. It is not possible to discern an exact relationship between these two parts, thus bringing out the final needed factor of \( \hbar \). However, a simple approximate relationship between the two parts was discovered by approximating a harmonic oscillator with nonlinear polarizability.
7.2 Relating TCFs $f$ and $g$

As demonstrated earlier with the one-time TCFs, it is useful to write $f(t_1, t_2)$ and $g(t_1, t_2)$ out in their energy representations as a means of finding a relationship between them. Carrying out this step then inserting three complete sets of states $\sum_i |i\rangle\langle i|$ with $H|i\rangle = E_i|i\rangle$ gives the following results. Manipulating the indices $i$, $j$, and $k$, equivalent to taking cyclic permutations of the trace, allows the similarities between TCFs $f$ and $g$ to be maximized. The only difference between them is the Boltzmann factor $e^{-\beta H}$.

$$f(t_1, t_2) = \frac{1}{Q} \sum_i \sum_j \sum_k e^{-\beta E_i \Pi_{ik} \Pi_{kj} \Pi_{ji} e^{it_1 E_{ki}/\hbar} e^{it_2 E_{kj}/\hbar}}$$

$$g(t_1, t_2) = \frac{1}{Q} \sum_i \sum_j \sum_k e^{-\beta E_k \Pi_{ik} \Pi_{kj} \Pi_{ji} e^{it_1 E_{ki}/\hbar} e^{it_2 E_{kj}/\hbar}}$$

(7.4)

Similarly, the complex conjugates can also be written in the energy representation. If the polarizability matrix elements are chosen real so that $\Pi_{ij} = \Pi_{ij}^*$, it is clear that $f^*(t_1, t_2) = f(-t_1, -t_2)$ and $g^*(t_1, t_2) = -g(-t_1, -t_2)$.

$$f^*(t_1, t_2) = \frac{1}{Q} \sum_i \sum_j \sum_k e^{-\beta E_i \Pi_{ik} \Pi_{kj} \Pi_{ji} e^{it_1 E_{ki}/\hbar} e^{it_2 E_{kj}/\hbar}}$$

$$g^*(t_1, t_2) = \frac{1}{Q} \sum_i \sum_j \sum_k e^{-\beta E_k \Pi_{ik} \Pi_{kj} \Pi_{ji} e^{it_1 E_{ki}/\hbar} e^{it_2 E_{kj}/\hbar}}$$

(7.5)

A double Fourier transform converts the TCFs to the frequency domain, giving $f(\omega_1, \omega_2)$ and $g(\omega_1, \omega_2)$. It is easy to prove that $FT[f^*(t_1, t_2)] = f(-\omega_1, -\omega_2)$ and $FT[g^*(t_1, t_2)] = g(-\omega_1, -\omega_2)$. The proof is outlined below. The final step of the proof arises since the frequency-domain TCFs are real, implying that $f^*(\omega_1, \omega_2) = f(\omega_1, \omega_2)$.  

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\begin{align*}
  f(\omega_1, \omega_2) &= \left(\frac{1}{2\pi}\right)^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-i\omega_1 t_1} e^{-i\omega_2 t_2} f(t_1, t_2) dt_1 dt_2 \\
  f(-\omega_1, -\omega_2) &= \left(\frac{1}{2\pi}\right)^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{i\omega_1 t_1} e^{i\omega_2 t_2} f(t_1, t_2) dt_1 dt_2 \\
  f(-\omega_1, -\omega_2) &= f^*(-\omega_1, -\omega_2) = \left(\frac{1}{2\pi}\right)^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-i\omega_1 t_1} e^{-i\omega_2 t_2} \times f^*(t_1, t_2) dt_1 dt_2 \quad (7.6)
\end{align*}

In the frequency domain, the four TCFs can be written in terms of simple delta functions.

\begin{align*}
  f(\omega_1, \omega_2) &= \frac{1}{Q} \sum_i \sum_j \sum_k e^{-\beta E_i \Pi_{ik} \Pi_{kj}} \delta(\omega_1 - E_{ki}/\hbar) \delta(\omega_2 - E_{kj}/\hbar) \\
  f(-\omega_1, -\omega_2) &= \frac{1}{Q} \sum_i \sum_j \sum_k e^{-\beta E_i \Pi_{ik} \Pi_{kj}} \delta(\omega_1 - E_{ik}/\hbar) \delta(\omega_2 - E_{jk}/\hbar) \\
  g(\omega_1, \omega_2) &= \frac{1}{Q} \sum_i \sum_j \sum_k e^{-\beta E_k \Pi_{ik} \Pi_{kj}} \delta(\omega_1 - E_{ki}/\hbar) \delta(\omega_2 - E_{kj}/\hbar) \\
  g(-\omega_1, -\omega_2) &= \frac{1}{Q} \sum_i \sum_j \sum_k e^{-\beta E_k \Pi_{ik} \Pi_{kj}} \delta(\omega_1 - E_{ik}/\hbar) \delta(\omega_2 - E_{jk}/\hbar) \quad (7.7)
\end{align*}

Since the TCFs \( f \) and \( g \) differ only in the Boltzmann factors weighting them, it is straightforward to derive frequency-domain relationships between them.

\begin{align*}
  f(\omega_1, \omega_2) &= e^{\beta E_k} e^{-\beta E_i} g(\omega_1, \omega_2) = e^{\beta E_k} g(\omega_1, \omega_2) \\
  f(-\omega_1, -\omega_2) &= e^{\beta E_i} e^{-\beta E_k} g(-\omega_1, -\omega_2) = e^{\beta E_i} g(\omega_1, \omega_2) \quad (7.8)
\end{align*}
Enforcing the delta functions in Equation 7.7 requires that $\omega_1 = E_{ki}/\hbar$ in positive frequency and $\omega_1 = E_{ik}/\hbar$ in negative frequency. This action allows the Boltzmann factors to be taken outside the summations and used to relate the pair of TCFs. This result gives the detailed-balance equations which will be used to relate TCFs $f$ and $g$ in positive and negative frequency.

$$f(\omega_1, \omega_2) = e^{\beta \omega_1} g(\omega_1, \omega_2)$$

$$f(-\omega_1, -\omega_2) = e^{-\beta \omega_1} g(-\omega_1, -\omega_2) \quad (7.9)$$

Another useful step is to consider the way in which the sums and differences of TCFs $f$ and $g$ are related. In positive frequency,

$$\frac{f(\omega_1, \omega_2) - g(\omega_1, \omega_2)}{f(\omega_1, \omega_2) + g(\omega_1, \omega_2)} = \frac{e^{\beta \omega_1} - 1}{e^{\beta \omega_1} + 1} \times \frac{g(\omega_1, \omega_2)}{g(\omega_1, \omega_2)} \quad (7.10)$$

Multiplying the ratio by $e^{-\beta \omega_1/2}/e^{-\beta \omega_1/2}$ gives a simple tanh relationship between the difference and the sum of $f$ and $g$. The relationship for negative frequency, derived in the same manner, is also shown.

$$f(\omega_1, \omega_2) - g(\omega_1, \omega_2) = \tanh(\beta \hbar \omega_1/2)[f(\omega_1, \omega_2) + g(\omega_1, \omega_2)]$$

$$f(-\omega_1, -\omega_2) - g(-\omega_1, -\omega_2) = -\tanh(\beta \hbar \omega_1/2)[f(-\omega_1, -\omega_2) + g(-\omega_1, -\omega_2)] \quad (7.11)$$

Using Equation 7.11, the frequency-domain fifth order response function can be written as shown.
\[ R^{(5)}(\omega_1, \omega_2) = \left( \frac{1}{\hbar^2} \right) \tanh(\beta \hbar \omega_1/2) \left[ f(\omega_1, \omega_2) + g(\omega_1, \omega_2) - f(-\omega_1, -\omega_2) - g(-\omega_1, -\omega_2) \right] \] (7.12)

Now, using Equation 7.9, it is possible to exactly eliminate TCF \( f \) from the \( R^{(5)} \) expression. Having the fifth-order Raman expression in terms of one quantum mechanical TCF, rather than two, will ultimately make its computation less expensive.

\[ R^{(5)}(\omega_1, \omega_2) = \left( \frac{1}{\hbar^2} \right) \tanh(\beta \hbar \omega_1/2) \left[ (1 + e^{\beta \hbar \omega_1}) g(\omega_1, \omega_2) - (1 + e^{-\beta \hbar \omega_1}) g(-\omega_1, -\omega_2) \right] \] (7.13)

### 7.3 Classical Limit of \( R^{(5)} \)

In the classical limit, where \( \hbar \omega << kT \), Equation 7.12 has a prefactor of \( \beta \hbar \omega_1/2 \), which cancels out \( 1/\hbar \). In this limit, expanding the exponentials out to first order results in \( \tanh(\beta \hbar \omega_1/2) \to \beta \hbar \omega_1/2 \), \( e^{\beta \hbar \omega_1} \to 1 + \beta \hbar \omega_1 \), and \( e^{-\beta \hbar \omega_1} \to 1 - \beta \hbar \omega_1 \).

\[ R^{(5)}(\omega_1, \omega_2) = \left( \frac{1}{\hbar^2} \right) (\beta \hbar \omega_1/2) \left[ (2 + \beta \hbar \omega_1) g(\omega_1, \omega_2) - (2 - \beta \hbar \omega_1) g(-\omega_1, -\omega_2) \right] \] (7.14)

Equation 7.14 can be rewritten in terms of the Fourier transforms of the real and imaginary parts of TCF \( g(t_1, t_2) \). To accomplish this, consider the relationships
\[ g(\omega_1, \omega_2) + g(-\omega_1, -\omega_2) = 2g_R(\omega_1, \omega_2) \text{ and } g(\omega_1, \omega_2) - g(-\omega_1, -\omega_2) = 2g_I(\omega_1, \omega_2). \] The classical limit \( R^{(5)} \) expression then becomes

\[
R^{(5)}(\omega_1, \omega_2) = \left( \frac{1}{\hbar^2} \right) (\beta \hbar \omega_1 / 2)[4g_I(\omega_1, \omega_2) + 2\beta \hbar \omega_1 g_R(\omega_1, \omega_2)] \quad (7.15)
\]

In the time domain, the \( R^{(5)} \) expression in the classical limit can be written in terms of time derivatives of \( g(t_1, t_2) \).

\[
R^{(5)}(t_1, t_2) = -\beta^2 \frac{d^2}{dt_1^2} g_R(t_1, t_2) - \frac{2i\beta}{\hbar} \frac{d}{dt_1} g_I(t_1, t_2) \quad (7.16)
\]

### 7.4 Applying a Harmonic Approximation

In Equation 7.15, both \( \hbar \) prefactors are cancelled out in \( g_R \), but in \( g_I \), one \( 1/\hbar \) still remains. Consequently, \( g_R \) can be calculated in the classical limit as the classical TCF \( \langle \Pi(0) \Pi(-t_1) \Pi(t_2) \rangle \), but \( g_I \) has no apparent classical limit. For the entire expression to be valid in the classical limit, it is useful to find a relationship between \( g_R \) and \( g_I \) in order to remove this \( \hbar \). As seen in the previous chapter, the one-time correlation function \( C(t) \) exhibits a simple frequency-domain relationship between the Fourier transforms of the real and imaginary parts, \( C_I(\omega) = \text{tanh}(\beta \hbar \omega / 2)C_R(\omega) \). To begin deriving a similar relationship for \( g(t_1, t_2) \), an approximation must be considered.

An approximate connection between \( g_R \) and \( g_I \) can be established using a harmonic reference system with a nonlinear polarizability, the lowest order system that produces a fifth order response.
The harmonic system is represented by a harmonic potential of the form $V = m\Omega^2q^2/2$, where $\Omega$ is a fundamental harmonic frequency and $q$ is the harmonic coordinate. Harmonic states are assumed, and energies are harmonic, i.e. $E_\alpha = \beta\hbar\Omega(\alpha + 1/2)$.

The polarizability matrix elements in the frequency-domain TCFs, as shown in Equation 7.7, are expanded out to second order in the harmonic coordinate.

$$\Pi_{ij} = \Pi^0\delta_{ij} + \Pi'\langle i|q|j \rangle + \frac{1}{2}\Pi''\langle i|q^2|j \rangle$$ (7.17)

In Equation 7.17, the primes represent derivatives with respect to the harmonic coordinate. $\Pi^0$ is the static polarizability. The matrix elements in terms of the harmonic coordinate are written as follows.

$$\langle i|q|j \rangle = \sqrt{\frac{\hbar}{2m\Omega}} \times [\delta_{i,j+1}(i + 1)^{1/2} + \delta_{i,j-1}j^{1/2}]$$

$$\langle i|q^2|j \rangle = \frac{\hbar}{2m\Omega} \times [\delta_{i,j+2}((j + 1)(j + 2))^{1/2} + 2\delta_{ij}(j + \frac{1}{2}) + \delta_{i,j-2}[j(j - 1)]^{1/2}]$$ (7.18)

When the polarizability matrix elements in TCF $g$ are expanded according to Equation 7.17, TCF $g$ is split into several terms, which will be designated $g^{abc}$, where $a$, $b$, and $c$ represent the order to which each polarizability element is taken. For example, $g^{000}$ is written in terms of three $\Pi^0$ elements.

The first term to consider, $g^{000}$, is written as shown below.
\[
g(\omega_1, \omega_2)^{000} = \frac{1}{Q} (\Pi^0)^3 \sum_k e^{-\beta E_k} \tag{7.19}
\]

In the time domain, the derivative \(dg^{000}/dt_1 = 0\), implying by Equation 7.16 that the \(g^{000}\) term does not contribute to \(R^{(5)}\). Next, the terms \(g^{001}\), \(g^{010}\), and \(g^{100}\), each of which have one \(\Pi'\) and two \(\Pi^0\) elements, are considered. Writing out the matrix elements and enforcing the included delta functions demonstrates that all three of these terms are zero, and can therefore do not need to be included in the expansion of \(g(\omega_1, \omega_2)\). By the same logic, the \(g^{111}\) is excluded from the \(R^{(5)}\) expression.

The next terms to consider are the ones containing two \(\Pi'\) and one \(\Pi^0\), namely \(g^{011}\), \(g^{101}\), and \(g^{110}\). These terms are shown below.

\[
g^{011}(\omega_1, \omega_2) = \Pi^0 \Pi' \Pi' \left( \frac{\hbar}{2m\Omega} \right) \left( \frac{1}{1 - e^{-\beta \hbar \Omega}} \right) \times
\quad \left[ e^{-\beta \hbar \Omega} \delta(\omega_2 - \Omega) + \delta(\omega_2 + \Omega) \right]
\]

\[
g^{101}(\omega_1, \omega_2) = \Pi^0 \Pi' \Pi' \left( \frac{\hbar}{2m\Omega} \right) \left( \frac{1}{1 - e^{-\beta \hbar \Omega}} \right) \times
\quad \left[ e^{-\beta \hbar \Omega} \delta(\omega_1 - \Omega) + \delta(\omega_1 + \Omega) \right]
\]

\[
g^{110}(\omega_1, \omega_2) = \Pi^0 \Pi' \Pi' \left( \frac{\hbar}{2m\Omega} \right) \left( \frac{1}{1 - e^{-\beta \hbar \Omega}} \right) \times
\quad \left[ e^{-\beta \hbar \Omega} \delta(\omega_1 + \Omega) \delta(\omega_2 + \Omega) + \delta(\omega_1 + \Omega) \delta(\omega_2 + \Omega) \right] \tag{7.20}
\]
For term $g^{011}$ the $t_1$ derivatives are zero, preventing it from contributing to the final expression. The other two terms are excluded because $R^{(5)}$ is calculated in terms of polarizability fluctuations $\Delta \Pi$, meaning that contributions from static polarizability are eliminated by construction. Therefore, the only terms left to consider are the ones containing two $\Pi''$ and one $\Pi'$, which are $g^{211}$, $g^{121}$, and $g^{112}$. The total contribution to $g(\omega_1, \omega_2)$ of the first nonvanishing order is

$$g(\omega_1, \omega_2) = g^{211}(\omega_1, \omega_2) + g^{121}(\omega_1, \omega_2) + g^{112}(\omega_1, \omega_2) \tag{7.21}$$

Given Equation 7.21, it is useful to derive relationships between the real and imaginary parts of all three terms and attempt to generalize the relationship to the entire TCF. To derive each term, the $\Pi$ matrix elements are written out, the delta functions are enforced, and the geometric series given by the sums evaluated.

As an illustration, term $g^{211}$ is shown below in the frequency domain.

$$g^{211}(\omega_1, \omega_2) = \Pi''\Pi'\Pi Q \left( \frac{\hbar}{2m\Omega} \right)^2 \frac{1}{2} \times 
\sum_k (e^{-\beta\hbar\Omega})^k [(k + 1)(k + 2)\delta(\omega_1 + 2\Omega)\delta(\omega_2 + \Omega) +\n(k + 1)(2k + 1)\delta(\omega_1)\delta(\omega_2 + \Omega) + \n2k(2k + 1)\delta(\omega_1)\delta(\omega_2 - \Omega) + \nk(k - 1)\delta(\omega_1 - 2\Omega)\delta(\omega_2 - \Omega)] \tag{7.22}$$

To relate its real and imaginary parts, it is necessary to reverse Fourier transform $g^{211}$ to the time domain.
\[ g^{211}(t_1, t_2) = \Pi'' \Pi' \left( \frac{\hbar}{2m \Omega} \right)^2 \left[ \frac{1}{(1 - e^{-\beta \hbar \Omega})^2} \right] \times \]

\[ \left[ 2e^{-2\beta \hbar \Omega} e^{-\beta \hbar \Omega} + (3e^{-\beta \hbar \Omega} + 1)e^{-\beta \hbar \Omega} + \\
(3e^{-\beta \hbar \Omega} + e^{-2\beta \hbar \Omega}) e^{-\beta \hbar \Omega} + 2e^{-2\beta \hbar \Omega} e^{2\beta \hbar \Omega} e^{\beta \hbar \Omega} \right] \]

(7.24)

To derive the real part \( B_R^{211}(t_1, t_2) \), the complex conjugate is added to Equation 7.24, and to derive the imaginary part \( B_I^{211}(t_1, t_2) \), the complex conjugate is subtracted. The complex conjugate is determined by changing all \( i \) to \(-i\).

\[ g_R^{211}(t_1, t_2) = \Pi'' \Pi' \left( \frac{\hbar}{2m \Omega} \right)^2 \left[ \frac{1}{4 (1 - e^{-\beta \hbar \Omega})^2} \right] \times \]

\[ \left[ (2 + 2e^{-2\beta \hbar \Omega}) \cos(2\Omega t_1 + \Omega t_2) + (e^{-2\beta \hbar \Omega} + 6e^{-\beta \hbar \Omega} + 1) \cos(\Omega t_2) \right] \]

\[ g_I^{211}(t_1, t_2) = \Pi'' \Pi' \left( \frac{\hbar}{2m \Omega} \right)^2 \left[ \frac{1}{4 (1 - e^{-\beta \hbar \Omega})^2} \right] \times \]

\[ \left[ (2e^{-2\beta \hbar \Omega} - 2) \sin(2\Omega t_1 + \Omega t_2) + (e^{-2\beta \hbar \Omega} - 1) \sin(\Omega t_2) \right] \]

(7.25)

Similar manipulations can be used to derive the real and imaginary parts of the \( g^{121} \) and \( g^{112} \) terms.

\[ g_R^{121}(t_1, t_2) = \Pi'' \Pi' \left( \frac{\hbar}{2m \Omega} \right)^2 \left[ \frac{1}{4 (1 - e^{-\beta \hbar \Omega})^2} \right] \times \]

\[ \left[ (2 + 2e^{-2\beta \hbar \Omega}) \cos(\Omega t_1 + 2\Omega t_2) + (e^{-2\beta \hbar \Omega} + 6e^{-\beta \hbar \Omega} + 1) \cos(\Omega t_1) \right] \]
\[ g_{I}^{121}(t_1, t_2) = \Pi''\Pi'\Pi'\left(\frac{\hbar}{2m\Omega}\right)^2 \frac{1}{4} \left[ \frac{1}{(1 - e^{-\beta\hbar\Omega})^2} \right] \times \]
\[ (2e^{-2\beta\hbar\Omega} - 2) \sin(\Omega t_1 + 2\Omega t_2) + (e^{-2\beta\hbar\Omega} - 1) \sin(\Omega t_1) \]

\[ g_{R}^{112}(t_1, t_2) = \Pi''\Pi'\Pi'\left(\frac{\hbar}{2m\Omega}\right)^2 \frac{1}{4} \left[ \frac{1}{(1 - e^{-\beta\hbar\Omega})^2} \right] \times \]
\[ [4e^{-\beta\hbar\Omega} \cos(\Omega t_1 - \Omega t_2) + (3e^{-2\beta\hbar\Omega} + 2e^{-\beta\hbar\Omega} + 3) \cos(\Omega t_1 + \Omega t_2)] \]

\[ g_{I}^{112}(t_1, t_2) = \Pi''\Pi'\Pi'\left(\frac{\hbar}{2m\Omega}\right)^2 \frac{1}{4} \left[ \frac{1}{(1 - e^{-\beta\hbar\Omega})^2} \right] \times \]
\[ [(3e^{-2\beta\hbar\Omega} - 3) \sin(\Omega t_1 + \Omega t_2)] \] (7.26)

7.5 Removing \(g_I\) from the \(R^{(5)}\) Expression

The three contributions to TCF \(g\) can each be split into two terms with distinct time or frequency dependence, yielding a total of six contributions to \(g\). Each should offer an order \(\hbar\) relationship between its real and imaginary parts. To obtain a classical result, the relationship for all six terms must be of the same form, as the distinct contributions cannot be distinguished during the course of a classical molecular dynamics simulation.

While no single expression works perfectly for all six terms, it has been determined that the following tanh relationship is a satisfactory approximation in the classical limit and leads to a TCF theory for \(R^{(5)}\) that has reasonable limiting behavior.

\[ g_I(\omega_1, \omega_2) = \tanh(-\beta\hbar(\omega_1/4 + \omega_2/2))g_R(\omega_1, \omega_2) \] (7.27)
In the classical limit, with exponentials expanded out to order $\hbar$, the tanh shown in Equation 7.27 becomes $-\beta\hbar(\omega_1/4 + \omega_2/4)$. Table 7.5 displays the limiting form of all frequency prefactors and the value of $-\beta\hbar(\omega_1/4 + \omega_2/4)$ for all terms, with $g_{211}^{\text{R}}$, $g_{121}^{\text{R}}$, and $g_{112}^{\text{R}}$ each split into its two parts. In the classical limit, for the proposed relationship in Equation 7.27 to be valid, multiplying the coefficient of $g_{\text{R}}$ by $-\beta\hbar(\omega_1/4 + \omega_2/4)$ should yield the coefficient of $g_{I}$. For three terms, the proposed tanh relationship gives the exact desired results, and it comes very close for the other three. To illustrate how the coefficients are defined, coefficients $C_1$ and $C_2$ for term $g_{\text{R}}^{211}$ are written below.

\[
g_{\text{R}}^{211}(t_1, t_2) = \Pi''\Pi'\Pi' \left( \frac{\hbar}{2m\Omega} \right)^2 \frac{1}{4} \left[ \frac{1}{1 - e^{-\beta\hbar\Omega}} \right]^2 \times \left[ C_1 \cos(2\Omega t_1 + \Omega t_2) + C_2 \cos(\Omega t_2) \right]
\]

\[
C_1 = 2 + 2e^{-2\beta\hbar\Omega} \quad C_2 = e^{-2\beta\hbar\Omega} + 6e^{-\beta\hbar\Omega} + 1 \quad (7.28)
\]

For the three terms which are not accurately described by the tanh relationship, errors in “filtering the dynamics” are introduced into the calculations. In spite of this inaccuracy, this approximation has been used to produce results for liquid xenon which are in nearly quantitative agreement with exact numerical calculations.\textsuperscript{43-45}

In the classical limit, the tanh relationship is applied to Equation 7.14 to obtain the fifth-order response function in terms of $g_{\text{R}}(\omega_1, \omega_2)$ alone.

\[
R^{(5)}(\omega_1, \omega_2) = \left( \frac{1}{\hbar^2} \right) \left( \frac{\beta\hbar\omega_1}{2} \right) [\beta\hbar\omega_1 - 2\beta\hbar\omega_2]g_{\text{R}}(\omega_1, \omega_2) \quad (7.29)
\]
Term 1
\[ g_{211} \]
\[ g_{121} \]
\[ g_{112} \]

Term 2
\[ g_{211} \]
\[ g_{121} \]
\[ g_{112} \]

Table 7.1: The usefulness of the relationship
\[ g_I(\omega_1, \omega_2) = -\tanh[\beta \hbar(\omega_1/4 + \omega_2/2)]g_R(\omega_1, \omega_2) \]
for a harmonic reference system is demonstrated. The six terms of the TCF \( g(\omega_1, \omega_2) \) are displayed. In the classical limit, this \( \tanh \) relationship dictates that the \( g_R \) coefficient (column 2) multiplied by \( -\tanh[\beta \hbar(\omega_1/4 + \omega_2/2)] \) (column 6) should give the \( g_I \) coefficient (column 3). This relationship holds exactly for \( g_{111} \) Term 1, \( g_{121} \) Term 2, and \( g_{112} \) Term 2, and very nearly for the remaining three terms.
In the time domain, this expression is written out in terms of time derivatives of $g_R(t_1, t_2)$, a TCF which can, in the classical limit, be calculated using molecular dynamics techniques.

$$R^{(5)}(t_1, t_2) = -\frac{\beta^2}{2} \left[ \frac{d^2}{dt_1^2} g_R(t_1, t_2) - 2 \frac{d^2}{dt_2^2} g_R(t_1, t_2) \right]$$  \hspace{1cm} (7.30)
Probing the three-dimensional structure of molecules, particularly complex proteins, peptides, and other biomolecules, is an important objective in many spectroscopic investigations. In the case of proteins, the three-dimensional structure is a direct reflection of the molecule’s function. Experimentally determining the three-dimensional structure of transient species in condensed phases is difficult but essential to understanding the nature of many interesting time-dependent processes, such as protein folding. Traditional experimental techniques including multidimensional nuclear magnetic resonance (NMR) spectroscopy\textsuperscript{46–49} and X-Ray diffraction\textsuperscript{50, 51} work on millisecond time scales and effectively reveal time-averaged three-dimensional structures. However, since many systems are transient, such as proteins, whose conformations often fluctuate several times on this time scale, these techniques often fail to accurately describe short-lived species.

Two-dimensional infrared (2D-IR) spectroscopy, a technique currently under extensive theoretical and experimental investigation, shows great potential for providing new information about time evolving structures.\textsuperscript{52–56} Unlike multidimensional NMR and X-Ray diffraction, 2D-IR can approach a time scale on the order of picoseconds or even femtoseconds. Additionally, 2D-IR is capable of resolving the structures of complex
molecules, whose linear spectra are often extremely congested and difficult to interpret. Couplings, revealed as pairs of cross-peaks in 2D-IR spectra, are suggestive of the relative orientations of pairs of coupled anharmonic oscillators and consequently hint at the system’s three-dimensional structure.

The scientific community has recognized 2D-IR’s adaptability to many interesting applications. 2D-IR techniques have already proven useful in examining the coupled carbonyl stretches of $\text{Rh(CO)}_2(\text{C5H7O2})$, the nuclear potential energy surface of coupled molecular vibrations, vibrational relaxation, interactions between solvent and solute, conforational fluctuations in peptides, the three-dimensional structure of peptides and small proteins, the hydrogen bond network in water, and the coupling of cytidine and guanosine in DNA. 2D-IR spectroscopy can be used to determine the coupling and projection angle between two anharmonic vibrations.

In this chapter, a time correlation function (TCF) theory of two-dimensional infrared spectroscopy is developed. This theory allows the calculation of a system’s third order nonlinear response function $R^{(3)}(t_1, t_2, t_3)$ associated with 2D-IR from classical molecular dynamics (MD) trajectories. It is possible to calculate a single classical TCF $B_R(t_1, t_2, t_3) = \langle \mu_j(t_2 + t_1)\mu_i(t_3 + t_2 + t_1)\mu_k(t_1)\mu_\ell(0) \rangle$, Fourier transform, multiply by a set of a frequency factors, then back transform the result to obtain the time-domain response function. Finally, $R^{(3)}(t_1, t_2, t_3)$ may be convoluted with a series of electric input fields to obtain the third-order polarization $P^{(3)}$ which generates the 2D-IR signal.
A two-dimensional infrared (2D-IR) experiment measures the third-order non-linear polarization of a chemical system. In resonant 2D-IR experiments, three input electric fields $E_\alpha$, $E_\beta$, and $E_\gamma$, associated with wavevectors $k_\alpha$, $k_\beta$, and $k_\gamma$, cross the material of interest, described by its third-order response function $R^{(3)}$, to generate a third-order polarization $P^{(3)}$. The resulting field radiates in the phase-matched direction $k_s = -k_\alpha + k_\beta + k_\gamma$. The time ordering of fields $E_\alpha$, $E_\beta$, and $E_\gamma$ may be varied, allowing $k_s$ to originate from one of three possible wave matching conditions: $-k_1 + k_2 + k_3$, $k_1 - k_2 + k_3$, or $k_1 + k_2 - k_3$. The polarization $P^{(3)}_i$ at time $t$ is the convolution of the third-order response function $R^{(3)}$ with the three input fields, shown below as $E_{1\ell}$, $E_{2k}$, and $E_{3j}$.\[34, 91, 92\]

\[
P^{(3)}_i(t_1, t_2, t) = \int_0^\infty \int_0^\infty \int_0^\infty R^{(3)}_{ijk\ell}(t_1, t_2, t_3)E_{3j}(t - t_3)E_{2k}(t + \tau_2 - t_3 - t_2) \times \nonumber \\
E_{1\ell}(t + \tau_1 + \tau_2 - t_3 - t_2 - t_1)dt_1dt_2dt_3 \quad (8.1)
\]

In Equation 8.1, $t$ is the time elapsed after the final laser pulse, $\tau_1$ is the time delay between the first and second pulses, and $\tau_2$ is the time delay between the second and third pulses. The $t_n$ represent time intervals between the field-matter interactions and equal the $\tau_n$ if the pulse durations are significantly shorter than the time scale of the dynamics. The subscripts indicate laboratory Cartesian directions ($x$, $y$, $z$). In a vibrational echo 2D-IR experiment, the delay $t_2$ is typically set to zero.\[34, 63\] $R^{(3)}$, shown below in Equation 8.2, is the third-order response function associated with a resonant
The third order response function $R^{(3)}$ is a fourth rank tensor and depends on the polarization components $i, j, k, \ell$ of the incident fields.

$$R^{(3)}(t_1, t_2, t_3) = \left(\frac{-i}{\hbar}\right)^3 \langle [[[\mu_i(t_3 + t_2 + t_1), \mu_j(t_2 + t_1)], \mu_k(t_1)], \mu_\ell(0)] \rangle$$ \hspace{1cm} (8.2)

The $\mu$ represent the dipole moment operators in the subscripted Cartesian direction. The time-dependent dipole may be written as the Heisenberg representation of the operator, $\mu(t) = e^{iHt/\hbar}\mu e^{-iHt/\hbar}$. The square and angle brackets indicate commutators and quantum mechanical averages respectively in a standard notation.\(^{30}\)

Evaluation of the third-order response function as written is difficult due to the prohibitive computational expense of calculating four distinct four-point quantum mechanical TCFs. Even in the classical limit, the commutators become Poisson brackets of the dynamical variables, which are also impractical to evaluate computationally.\(^{41,43}\) To make $R^{(3)}(t_1, t_2, t_3)$ amenable to classical molecular dynamics computational methods, it is desirable to rewrite it in terms of the real part of a single TCF.

### 8.2 Introduction to the 2D-IR TCF Theory

As discussed in Chapters 6 and 7, theoretical methods that approximately relate quantum mechanical and classical time correlation functions have been used successfully for both one-time\(^{17,19,31-34,93-95}\) and two-time\(^{44,45,96}\) correlation functions. A similar method will be employed to simplify the $R^{(3)}$ expression and obtain an approximate TCF theory of the third order response function and two-dimensional infrared spectroscopy.
Expanding the nested commutators in Equation 8.2 yields four distinct quantum mechanical TCFs and their complex conjugates. One important objective in developing the TCF theory is to simplify the expression to be written in terms of only one of these TCFs. Additionally, a theory written in terms of a single time correlation function must have a classical limit of order $\hbar^0$. Thus, another objective is to eliminate the $i/\hbar^3$ prefactor while relating and eliminating TCFs.

It is possible to eliminate one $\hbar$ prefactor and rewrite the third-order response function in terms of two TCFs, $A(t_1, t_2, t_3)$ and $B(t_1, t_2, t_3)$, by employing exact frequency-domain detailed-balance relationships between pairs of quantum mechanical TCFs appearing in the $R^{(3)}$ expression.

Unfortunately, no exact means of eliminating the final two $\hbar$ and an additional TCF has been found. However, these simplifications may be accomplished by resorting to approximations. One approximation, which was used with success in developing the $R^{(5)}$ TCF theory, is based on a model system of a harmonic oscillator with a linearly varying dipole. Once the approximation is applied, a general relationship between the remaining two TCFs becomes apparent, and the expression is derived in terms of the real and imaginary parts of a single TCF, $B(t_1, t_2, t_3)$. Finally, a relationship between the real and imaginary parts of $B(t_1, t_2, t_3)$ is employed to obtain an $R^{(3)}$ expression which may be calculated using classical molecular dynamics.

The resulting expression is exact for a harmonic system and can be applied to fully anharmonic dynamics using classical MD techniques. It is important to note that a harmonic oscillator with a linearly varying dipole gives no two-dimensional infrared
signal. Thus, this version of the TCF theory serves to “filter out” harmonic dynamics and enhance the anharmonic couplings in the signal.\textsuperscript{63}

Since anharmonic dynamics and couplings are essential to the interpretation of 2D-IR spectra,\textsuperscript{63,82} the development of the $R^{(3)}$ TCF theory using a different reference system to relate the TCFs is appropriate. An anharmonic reference system, represented as a harmonic system treated with a cubic perturbation,\textsuperscript{97} was used in developing another version of the $R^{(3)}$ theory.

### 8.3 Expansion of the $R^{(3)}$ Expression

The $R^{(3)}$ expression in Equation 8.2 contains a trace of nested commutators, which must be imaginary and have a leading contribution of order $\hbar^3$ in order to cancel the $i/\hbar^3$ prefactor. Expanding the commutators shown in Equation 8.2 yields an expression in terms of four four-point dipole time correlation functions and their complex conjugates, as demonstrated below in Equation 8.3. Because the dipole moment operators commute classically, the four TCFs defined in Equation 8.4 are expected have the same classical limit.

\[
R_{ijk\ell}^{(3)}(t_1, t_2, t_3) = \left(-\frac{i}{\hbar}\right)^3 \left[ A(t_1, t_2, t_3) - B(t_1, t_2, t_3) - C^*(t_1, t_2, t_3) + D^*(t_1, t_2, t_3) \right.
\]

\[
- D(t_1, t_2, t_3) + C(t_1, t_2, t_3) + B^*(t_1, t_2, t_3) - A^*(t_1, t_2, t_3) \right] \quad (8.3)
\]
\[ A(t_1, t_2, t_3) = \langle \mu_i(t_1 + t_2 + t_3)\mu_j(t_2 + t_1)\mu_k(t_1)\mu_\ell(0) \rangle \]

\[ B(t_1, t_2, t_3) = \langle \mu_j(t_2 + t_1)\mu_i(t_1 + t_2 + t_3)\mu_k(t_1)\mu_\ell(0) \rangle \]

\[ C(t_1, t_2, t_3) = \langle \mu_\ell(0)\mu_j(t_2 + t_1)\mu_i(t_3 + t_2 + t_1)\mu_k(t_1) \rangle \]

\[ D(t_1, t_2, t_3) = \langle \mu_\ell(0)\mu_i(t_3 + t_2 + t_1)\mu_j(t_2 + t_1)\mu_k(t_1) \rangle \]

(8.4)

In Equation 8.3, the star superscripts represent the complex conjugates of the complex time domain TCFs. The contents of the square brackets may be seen as sums and differences of the imaginary parts of the four TCFs, namely \(2(A_I - B_I - C_I + D_I)\), since for a complex quantity \(C\), \(C - C^* = C_I\). The subscripts \(R\) or \(I\) denote the real and imaginary parts of a time domain TCF (or the Fourier transforms of the real and imaginary parts), respectively. After identifying the four time correlation functions, the next step is to form relationships between them in order to simplify the \(R^{(3)}\) expression.

### 8.4 The Energy Representation

To proceed with the simplification of \(R^{(3)}\) and also to verify the classical limit of the TCFs \(A\), \(B\), \(C\), and \(D\), it is helpful to rewrite them in the energy representation. For example, TCF \(A(t_1, t_2, t_3)\) written in the energy representation is shown below in Equation 8.5.
\[ A(t_1, t_2, t_3) = \langle \mu_i (t_3 + t_2 + t_1) \mu_j (t_2 + t_1) \mu_k (t_1) \mu_\ell \rangle \]

\[ A(t_1, t_2, t_3) = \frac{1}{Q} \sum_a \langle a | e^{-\beta H} e^{iH(t_1+t_2+t_3)/\hbar} \mu e^{-iH(t_1+t_2+t_3)/\hbar} \times \]
\[ e^{iH(t_1+t_2)/\hbar} \mu_j e^{-iH(t_1+t_2)/\hbar} e^{iHt_1/\hbar} \mu_k e^{-iHt_1/\hbar} \mu_\ell | a \rangle \]  

(8.5)

In the energy representation, the dipole moment operators are multiplied by \( \rho = e^{-\beta H}/Q \), where \( Q \) is the partition function, and the trace is taken. The time-dependent dipoles are written in the Heisenberg representation, \( i.e. \mu_a(t) = e^{iHt/\hbar} \mu e^{-iHt/\hbar} \).

Next, inserting four complete sets of energy eigenstates of the form \( \sum_a |a \rangle \langle a | \) with \( H|a \rangle = E_a |a \rangle \), operating, and simplifying yields time-domain expressions of the following form:

\[ A(t_1, t_2, t_3) = \frac{1}{Q} \sum_{abcd} e^{-\beta E_{ab}} \mu_{ad} \mu_{ac} \mu_{cb} \mu_{bd} e^{iE_{ab}t_1/\hbar} e^{iE_{ac}t_2/\hbar} e^{iE_{cb}t_3/\hbar} \]  

(8.6)

In Equation 8.6, \( E_{ab} = E_a - E_b \) is the energy difference between states \( a \) and \( b \). The dipole moment operator matrix elements, \( \mu_{ab} = \langle a | \mu | b \rangle \), are Hermitian, \( i.e. \mu_{ij}^* = \mu_{ji} \). If the dipole moment operator matrix elements are taken as real, it clear that \( A^*(t_1, t_2, t_3) = A(-t_1, -t_2, -t_3) \). Comparison of Equations 8.6 and 8.7 verifies this claim.
\[ A^*(t_1, t_2, t_3) = \langle \mu(t_1) \mu(t_2) \mu(t_3) \rangle \]

\[ A^*(t_1, t_2, t_3) = A(-t_1, -t_2, -t_3) = \frac{1}{Q} \sum_{abcd} e^{-\beta E_{a\mu i}} \mu_{ad_{de\mu i}}^{j} \mu_{cb\mu i}^{k} e^{iE_{ba\mu i}} \hbar e^{iE_{ca\mu j}} \hbar e^{iE_{da\mu k}} \] (8.7)

The remaining three TCFs \( B(t_1, t_2, t_3) \), \( C(t_1, t_2, t_3) \), and \( D(t_1, t_2, t_3) \) can be written in a similar manner in the energy representation. Index switching, equivalent to taking cyclic permutations of the trace,\(^{52,96}\) is used to maximize the similarities between the TCFs. In Equation 8.8, these three TCFs are written in the time domain. Note that the pair of TCFs \( A(t_1, t_2, t_3) \) and \( D(t_1, t_2, t_3) \), as well as the pair \( B(t_1, t_2, t_3) \) and \( C(t_1, t_2, t_3) \) differ only by the Boltzmann factor \( e^{-\beta H} \).

\[ B(t_1, t_2, t_3) = \frac{1}{Q} \sum_{abcd} e^{-\beta E_{a\mu i}} \mu_{de\mu i}^{j} \mu_{cb\mu i}^{k} e^{iE_{ba\mu i}} \hbar e^{iE_{ca\mu j}} \hbar e^{iE_{da\mu k}} \]

\[ B^*(t_1, t_2, t_3) = \frac{1}{Q} \sum_{abcd} e^{-\beta E_{a\mu i}} \mu_{de\mu i}^{j} \mu_{cb\mu i}^{k} e^{iE_{ba\mu i}} \hbar e^{iE_{ca\mu j}} \hbar e^{iE_{da\mu k}} \]

\[ C(t_1, t_2, t_3) = \frac{1}{Q} \sum_{abcd} e^{-\beta E_{b\mu j}} \mu_{de\mu j}^{k} \mu_{cb\mu j}^{\ell} e^{iE_{ba\mu j}} \hbar e^{iE_{ca\mu k}} \hbar e^{iE_{da\mu \ell}} \]

\[ C^*(t_1, t_2, t_3) = \frac{1}{Q} \sum_{abcd} e^{-\beta E_{b\mu j}} \mu_{de\mu j}^{k} \mu_{cb\mu j}^{\ell} e^{iE_{ba\mu j}} \hbar e^{iE_{ca\mu k}} \hbar e^{iE_{da\mu \ell}} \]

\[ D(t_1, t_2, t_3) = \frac{1}{Q} \sum_{abcd} e^{-\beta E_{b\mu j}} \mu_{de\mu j}^{k} \mu_{cb\mu j}^{\ell} e^{iE_{ba\mu j}} \hbar e^{iE_{ca\mu k}} \hbar e^{iE_{da\mu \ell}} \]

\[ D^*(t_1, t_2, t_3) = \frac{1}{Q} \sum_{abcd} e^{-\beta E_{b\mu j}} \mu_{de\mu j}^{k} \mu_{cb\mu j}^{\ell} e^{iE_{ba\mu j}} \hbar e^{iE_{ca\mu k}} \hbar e^{iE_{da\mu \ell}} \] (8.8)
8.5 Frequency Domain TCFs

To derive analytical relationships between the TCFs, it is beneficial to perform the triple Fourier transform to obtain frequency domain functions of the form $A(\omega_1, \omega_2, \omega_3)$.

$$A(\omega_1, \omega_2, \omega_3) = \left(\frac{1}{2\pi}\right)^2 \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{\infty} dt_3 e^{-i\omega_1 t_1} e^{-i\omega_2 t_2} e^{-i\omega_3 t_3} A(t_1, t_2, t_3) \tag{8.9}$$

The four frequency-domain TCFs $A(\omega_1, \omega_2, \omega_3)$, $B(\omega_1, \omega_2, \omega_3)$, $C(\omega_1, \omega_2, \omega_3)$, and $D(\omega_1, \omega_2, \omega_3)$ are shown below in Equation 8.10.

$$A(\omega_1, \omega_2, \omega_3) = \frac{1}{Q} \sum_{abcd} e^{-\beta E_a} \mu^i_{ad} \mu^j_{dc} \mu^k_{cb} \mu^\ell_{ba} \delta(\omega_1 - E_{ab}/h) \delta(\omega_2 - E_{ac}/h) \delta(\omega_3 - E_{ad}/h)$$

$$B(\omega_1, \omega_2, \omega_3) = \frac{1}{Q} \sum_{abcd} e^{-\beta E_a} \mu^i_{dc} \mu^j_{ad} \mu^k_{cb} \mu^\ell_{ba} \delta(\omega_1 - E_{ab}/h) \delta(\omega_2 - E_{ac}/h) \delta(\omega_3 - E_{dc}/h)$$

$$C(\omega_1, \omega_2, \omega_3) = \frac{1}{Q} \sum_{abcd} e^{-\beta E_a} \mu^i_{ad} \mu^j_{dc} \mu^k_{cb} \mu^\ell_{ba} \delta(\omega_1 - E_{ab}/h) \delta(\omega_2 - E_{ac}/h) \delta(\omega_3 - E_{dc}/h)$$

$$D(\omega_1, \omega_2, \omega_3) = \frac{1}{Q} \sum_{abcd} e^{-\beta E_a} \mu^i_{ad} \mu^j_{dc} \mu^k_{cb} \mu^\ell_{ba} \delta(\omega_1 - E_{ab}/h) \delta(\omega_2 - E_{ac}/h) \delta(\omega_3 - E_{ad}/h) \tag{8.10}$$

It is straightforward to prove that the Fourier transforms of the complex conjugates of the four TCFs give the TCFs in negative frequency, i.e. $FT[f^*(t_1, t_2, t_3)] = f(-\omega_1, -\omega_2, -\omega_3)$. In general, the triple Fourier transform of a time-domain function $f(t_1, t_2, t_3)$ is defined as follows:
\[ FT[f(t_1, t_2, t_3)] = f(\omega_1, \omega_2, \omega_3) \]

\[
f(\omega_1, \omega_2, \omega_3) = \left(\frac{1}{2\pi}\right)^3 \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{\infty} dt_3 e^{-i\omega_1 t_1} e^{-i\omega_2 t_2} e^{-i\omega_3 t_3} \times f(t_1, t_2, t_3) \quad (8.11)
\]

All of the frequency arguments appearing in Equation 8.11 are made negative to obtain an expression for \( f(-\omega_1, -\omega_2, -\omega_3) \).

\[
f(-\omega_1, -\omega_2, -\omega_3) = \left(\frac{1}{2\pi}\right)^3 \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{\infty} dt_3 e^{i\omega_1 t_1} e^{i\omega_2 t_2} e^{i\omega_3 t_3} \times f(t_1, t_2, t_3) \quad (8.12)
\]

To finish the proof, the complex conjugate of both sides is taken. The right side of Equation 8.12 then becomes the triple Fourier transform of \( f^*(t_1, t_2, t_3) \). Consequently, \( FT[f^*(t_1, t_2, t_3)] = f^*(-\omega_1, -\omega_2, -\omega_3) \). Taking into account that the frequency domain TCFs are real, the final result is obtained:

\[
FT[f^*(t_1, t_2, t_3)] = f(-\omega_1, -\omega_2, -\omega_3)
\]

\[
f(-\omega_1, -\omega_2, -\omega_3) = \left(\frac{1}{2\pi}\right)^3 \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{\infty} dt_3 e^{-i\omega_1 t_1} e^{-i\omega_2 t_2} e^{-i\omega_3 t_3} \times f^*(t_1, t_2, t_3) \quad (8.13)
\]
The Fourier transforms of the complex conjugates of TCFs $A$, $B$, $C$, and $D$ are shown below in Equation 8.14.

\[
A(-\omega_1, -\omega_2, -\omega_3) = \frac{1}{Q} \sum_{abcd} e^{-\beta E_a} \mu^i_{da} \mu^j_{cd} \mu^k_{bc} \mu^\ell_{ab} \times \\
\delta(\omega_1 - E_{ba}/\hbar) \delta(\omega_2 - E_{ca}/\hbar) \delta(\omega_3 - E_{da}/\hbar)
\]

\[
B(-\omega_1, -\omega_2, -\omega_3) = \frac{1}{Q} \sum_{abcd} e^{-\beta E_b} \mu^i_{cd} \mu^j_{da} \mu^k_{bc} \mu^\ell_{ab} \times \\
\delta(\omega_1 - E_{ba}/\hbar) \delta(\omega_2 - E_{ca}/\hbar) \delta(\omega_3 - E_{cd}/\hbar)
\]

\[
C(-\omega_1, -\omega_2, -\omega_3) = \frac{1}{Q} \sum_{abcd} e^{-\beta E_b} \mu^i_{cd} \mu^j_{da} \mu^k_{bc} \mu^\ell_{ab} \times \\
\delta(\omega_1 - E_{ba}/\hbar) \delta(\omega_2 - E_{ca}/\hbar) \delta(\omega_3 - E_{cd}/\hbar)
\]

\[
D(-\omega_1, -\omega_2, -\omega_3) = \frac{1}{Q} \sum_{abcd} e^{-\beta E_b} \mu^i_{cd} \mu^j_{da} \mu^k_{bc} \mu^\ell_{ab} \times \\
\delta(\omega_1 - E_{ba}/\hbar) \delta(\omega_2 - E_{ca}/\hbar) \delta(\omega_3 - E_{da}/\hbar)
\]

(8.14)

8.6 Detailed-Balance Relationships

By visual inspection of Equation 8.10, it is easily observed that TCFs $A(\omega_1, \omega_2, \omega_3)$ and $D(\omega_1, \omega_2, \omega_3)$ are exactly the same, except for the Boltzmann factors $e^{-\beta E_a}$ and $e^{-\beta E_b}$. Some simple multiplication can be used to convert one of the two TCFs into the other.

\[
D(\omega_1, \omega_2, \omega_3) = e^{\beta E_a} e^{-\beta E_b} A(\omega_1, \omega_2, \omega_3)
\]

(8.15)

Enforcing the delta function $\delta(\omega_1 - E_{ab}/\hbar)$ (forcing $E_a - E_b = \hbar \omega_1$) allows Equation 8.15 to be rewritten in terms of $\omega_1$. 70
\[ D(\omega_1, \omega_2, \omega_3) = e^{\beta \hbar \omega_1} A(\omega_1, \omega_2, \omega_3) \]  

(8.16)

In negative frequency, an analogous relationship is derived.

\[ D(-\omega_1, -\omega_2, -\omega_3) = e^{-\beta \hbar \omega_1} A(-\omega_1, -\omega_2, -\omega_3) \]  

(8.17)

In a similar manner, the frequency domain TCFs \( B(\omega_1, \omega_2, \omega_3) \) and \( C(\omega_1, \omega_2, \omega_3) \) can be paired up and exact detailed-balance relationships can be derived between them and their negative frequency counterparts.

\[ C(\omega_1, \omega_2, \omega_3) = e^{\beta \hbar \omega_1} B(\omega_1, \omega_2, \omega_3) \]

\[ C(-\omega_1, -\omega_2, -\omega_3) = e^{-\beta \hbar \omega_1} B(-\omega_1, -\omega_2, -\omega_3) \]  

(8.18)

Using the previously derived detailed-balance relationships between TCF pairs, it is possible to derive simple tanh relationships between sums and differences of the TCFs. For example, consider TCFs \( A(\omega_1, \omega_2, \omega_3) \) and \( D(\omega_1, \omega_2, \omega_3) \).

\[ D(\omega_1, \omega_2, \omega_3) + A(\omega_1, \omega_2, \omega_3) = (e^{\beta \hbar \omega_1} + 1) A(\omega_1, \omega_2, \omega_3) \]

\[ D(\omega_1, \omega_2, \omega_3) + A(\omega_1, \omega_2, \omega_3) = (e^{\beta \hbar \omega_1} - 1) A(\omega_1, \omega_2, \omega_3) \]  

(8.19)

The ratio of \( D(\omega_1, \omega_2, \omega_3) - A(\omega_1, \omega_2, \omega_3) \) to \( D(\omega_1, \omega_2, \omega_3) + A(\omega_1, \omega_2, \omega_3) \) is shown below in Equation 8.20. Multiplying the ratio through by \( e^{-\beta \hbar \omega_1/2}/e^{-\beta \hbar \omega_1/2} \) reveals a tanh relationship between the sum and difference of \( A(\omega_1, \omega_2, \omega_3) \) and \( D(\omega_1, \omega_2, \omega_3) \).
\[
\frac{D(\omega_1, \omega_2, \omega_3) - A(\omega_1, \omega_2, \omega_3)}{D(\omega_1, \omega_2, \omega_3) + A(\omega_1, \omega_2, \omega_3)} = e^{\beta \hbar \omega_1} - 1 \over e^{\beta \hbar \omega_1} + 1 = \frac{e^{\beta \hbar \omega_1/2} - e^{-\beta \hbar \omega_1/2}}{e^{\beta \hbar \omega_1/2} + e^{-\beta \hbar \omega_1/2}} = \tanh(\beta \hbar \omega_1/2) \quad (8.20)
\]

In an analogous manner, three other useful tanh relationships can be derived. The four tanh relationships are summarized below in equation 8.21.

\[
D(\omega_1, \omega_2, \omega_3) - A(\omega_1, \omega_2, \omega_3) = \tanh(\beta \hbar \omega_1/2) [D(\omega_1, \omega_2, \omega_3) + A(\omega_1, \omega_2, \omega_3)]
\]

\[
D(-\omega_1, -\omega_2, -\omega_3) - A(-\omega_1, -\omega_2, -\omega_3) = -\tanh(\beta \hbar \omega_1) [D(-\omega_1, -\omega_2, -\omega_3) + A(-\omega_1, -\omega_2, -\omega_3)]
\]

\[
C(\omega_1, \omega_2, \omega_3) - B(\omega_1, \omega_2, \omega_3) = \tanh(\beta \hbar \omega_1/2) [C(\omega_1, \omega_2, \omega_3) + D(\omega_1, \omega_2, \omega_3)]
\]

\[
C(-\omega_1, -\omega_2, -\omega_3) - B(-\omega_1, -\omega_2, -\omega_3) = -\tanh(\beta \hbar \omega_1) [C(-\omega_1, -\omega_2, -\omega_3) + B(-\omega_1, -\omega_2, -\omega_3)] \quad (8.21)
\]

Using the detailed-balance and tanh relationships, it is possible to eliminate one \(\hbar\) prefactor, as well as the TCFs \(C\) and \(D\), from the \(R^{(3)}\) expression. The frequency domain third-order response is written below in its original form.
\[
R^{(3)}(\omega_1, \omega_2, \omega_3) = \left(\frac{-i}{\hbar}\right)^3 \left[ A(\omega_1, \omega_2, \omega_3) - D(\omega_1, \omega_2, \omega_3) + C(\omega_1, \omega_2, \omega_3) - B(\omega_1, \omega_2, \omega_3) + D(-\omega_1, -\omega_2, -\omega_3) - A(-\omega_1, -\omega_2, -\omega_3) + B(-\omega_1, -\omega_2, -\omega_3) - C(-\omega_1, -\omega_2, -\omega_3) \right] \tag{8.22}
\]

The tanh relationships are first employed to rewrite the differences between TCF pairs as sums.

\[
R^{(3)}(\omega_1, \omega_2, \omega_3) = \left(\frac{i}{\hbar^3}\right) \tanh(\beta \hbar \omega_1/2) \left[ A(\omega_1, \omega_2, \omega_3) + D(\omega_1, \omega_2, \omega_3) + B(\omega_1, \omega_2, \omega_3) + C(\omega_1, \omega_2, \omega_3) - A(-\omega_1, -\omega_2, -\omega_3) - D(-\omega_1, -\omega_2, -\omega_3) - B(-\omega_1, -\omega_2, -\omega_3) - C(-\omega_1, -\omega_2, -\omega_3) \right] \tag{8.23}
\]

Next, the detailed-balance relationships shown in Equations 8.16, 8.17, and 8.18 are used to rewrite the response function in terms of TCFs \(A\) and \(B\) only.

\[
R^{(3)}(\omega_1, \omega_2, \omega_3) = \left(\frac{i}{\hbar^3}\right) \tanh(\beta \hbar \omega_1/2) \times \left\{ (1 + e^{\beta \hbar \omega_1})[B(\omega_1, \omega_2, \omega_3) - A(\omega_1, \omega_2, \omega_3)] + (1 + e^{-\beta \hbar \omega_1})[B(-\omega_1, -\omega_2, -\omega_3) - A(-\omega_1, -\omega_2, -\omega_3)] \right\} \tag{8.24}
\]
The third-order response is now written in terms of two TCFs. No approximations have been invoked to obtain Equation 8.24. This equation indicates that the value of \( R^{(3)} \) is zero along the \( \omega_1 = 0 \) axis.

### 8.7 The Classical Limit of \( R^{(3)} \)

To demonstrate how one \( \hbar \) prefactor can be eliminated from the third-order response function, the classical limit, where \( \beta \hbar \omega_1 \) becomes small, is considered. In this limit, the tanh functions and exponentials can be expanded, retaining terms of order \( \hbar \).

\[
e^{\beta \hbar \omega_1} \to 1 + \beta \hbar \omega_1
\]

\[
e^{-\beta \hbar \omega_1} \to 1 - \beta \hbar \omega_1
\]

\[
tanh(\beta \hbar \omega_1/2) \to \beta \hbar \omega_1/2 \quad (8.25)
\]

Using Equation 8.25, the \( R^{(3)} \) expression displayed in Equation 8.24 can be rewritten, as shown below.

\[
R^{(3)}(\omega_1, \omega_2, \omega_3) = \left( \frac{i}{\hbar^3} \right) \left( \frac{\beta \hbar \omega_1}{2} \right) \{(2 + \beta \hbar \omega_1)[B(\omega_1, \omega_2, \omega_3) - A(\omega_1, \omega_2, \omega_3)] + (2 - \beta \hbar \omega_1)[B(-\omega_1, -\omega_2, -\omega_3) - A(-\omega_1, -\omega_2, -\omega_3)]\} \quad (8.26)
\]

It is easily proven that \( f^+ + f^- = 2f_R \) and \( f^+ - f^- = 2f_I \), where \( f^+ \) denotes a TCF in positive frequency, \( f^- \) a TCF in negative frequency, \( f_R \) the Fourier transform of \( f_R(t_1, t_2, t_3) \), and \( f_I \) the Fourier transform of \( f_I(t_1, t_2, t_3) \). Both \( f_R \) and \( f_I \) are themselves
real functions. These simple relationships allow the third-order response function to be rewritten again.

\[ R^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{i \beta \omega_1}{\hbar^2} (2B_R - 2A_R + \beta \hbar \omega_1 B_I - \beta \hbar \omega_1 A_I) \quad (8.27) \]

Examination of Equation 8.27 makes it clear that \( B_I - A_I \) must have a difference of order \( \hbar \) and \( B_R - A_I \) order \( \hbar^2 \) for the \( R^{(3)} \) expression to have a meaningful classical limit. Now, performing the reverse Fourier transform back to the time domain will give \( R^{(3)} \) in terms of time derivatives. In general, the following relationship holds true.

\[ \begin{align*}
  f(t_1, t_2, t_3) &= \int_{-\infty}^{\infty} e^{i\omega_1 t_1} e^{i\omega_2 t_2} e^{i\omega_3 t_3} f(\omega_1, \omega_2, \omega_3) d\omega_1 d\omega_2 d\omega_3 \\
  \frac{d}{dt_1} f(t_1, t_2, t_3) &= \int_{-\infty}^{\infty} i \omega_1 e^{i\omega_1 t_1} e^{i\omega_2 t_2} e^{i\omega_3 t_3} f(\omega_1, \omega_2, \omega_3) d\omega_1 d\omega_2 d\omega_3 \\
  \frac{d^2}{dt_1^2} f(t_1, t_2, t_3) &= -\int_{-\infty}^{\infty} \omega_1^2 e^{i\omega_1 t_1} e^{i\omega_2 t_2} e^{i\omega_3 t_3} f(\omega_1, \omega_2, \omega_3) d\omega_1 d\omega_2 d\omega_3 \\
 \end{align*} \quad (8.28) \]

Using Equation 8.28, the third-order response function can be rewritten one more time in terms of \( t_1 \) derivatives.

\[ \begin{align*}
  R^{(3)}(t_1, t_2, t_3) &= \frac{2 \beta}{\hbar^2} \left[ \frac{d}{dt_1} B_R(t_1, t_2, t_3) - \frac{d}{dt_1} A_R(t_1, t_2, t_3) \right] + \\
  &\quad \frac{i \beta^2}{\hbar} \left[ \frac{d^2}{dt_1^2} A_I(t_1, t_2, t_3) - \frac{d^2}{dt_1^2} B_I(t_1, t_2, t_3) \right] \\
 \end{align*} \quad (8.29) \]

Equation 8.29 demonstrates clearly that one \( \hbar \) can be eliminated exactly from the third-order response function when the classical limit is invoked. At this point, it is
necessary to consider approximations to simplify $R^{(3)}$ sufficiently to make it amenable to computation \textit{via} classical molecular dynamics techniques.
In this chapter, the development of the TCF theory of two-dimensional infrared spectroscopy (2D-IR) is continued. In the previous chapter, it was demonstrated that the third-order response function responsible for the 2D-IR signal could be written exactly in terms of two four-point dipole time correlation functions \( A(t_1, t_2, t_3) \) and \( B(t_1, t_2, t_3) \).

Further simplification of the third-order response function is desirable for two reasons. First, the results of classical molecular dynamics (MD) calculations will allow the calculation of \( f_R(t_1, t_2, t_3) \), the real part of a TCF, but not \( f_I(t_1, t_2, t_3) \), the imaginary part. It is necessary to eliminate \( A_I(t_1, t_2, t_3) \) and \( B_I(t_1, t_2, t_3) \) to make the use of this theory with classical MD techniques feasible. Second, since the calculation of a four-time TCF is computationally demanding, it makes sense to rewrite the expression in terms of just one of the TCFs.

In developing a theory of fifth-order Raman spectroscopy, a harmonic approximation was successfully invoked to allow computation of the fifth-order response function \( R^{(5)} \). Based on the success of this approach, this approximation was applied to the 2D-IR TCF theory. The approximation made it possible to derive a relationship between the frequency-domain TCFs \( A(\omega_1, \omega_2, \omega_3) \) and \( B(\omega_1, \omega_2, \omega_3) \), thus eliminating TCF \( A \).
from the expression. Additionally, it allowed the expression to be rewritten in terms of $B_R(\omega_1, \omega_2, \omega_3)$. These simplifications created a means of calculating a 2D-IR signal using classical MD. $B_R(t_1, t_2, t_3)$ could be calculated, Fourier transformed, then multiplied by a set of frequency factors to obtain a frequency-domain 2D-IR signal.

9.1 The Harmonic Approximation with Linearly Varying Dipole

In using the harmonic approximation, a harmonic potential

$$V = m\Omega^2 q^2 / 2$$

(9.1)

is assumed. $\Omega$ indicates a fundamental harmonic frequency. Harmonic energies of the form $E_a = \beta \hbar \Omega (a + 1/2)$ are also assumed. The partition function appearing in all the TCFs takes the following form.

$$Q = \frac{e^{-\beta \hbar \Omega / 2}}{1 - e^{-\beta \hbar \Omega}}$$

(9.2)

Additionally, the dipole moment matrix elements in the TCFs are expanded out to first order in the harmonic coordinate $q$ as shown.

$$\mu_{ij} = \mu^0 \delta_{ij} + \mu' q_{ij}$$
The $q_{ij}$ matrix elements are given by the expression

$$ q_{ij} = \left( \frac{\hbar}{2m\Omega} \right)^{1/2} \left[ \delta_{i,j+1}(j+1)^{1/2} + \delta_{i,j-1}j^{1/2} \right] $$

(9.3)

In Equation 9.3 the primes denote derivatives with respect to the harmonic coordinate $q$.

9.2 Applying the Approximation to $R^{(3)}$

Expansion of the four dipole moment matrix elements in TCFs $A$ and $B$ yields a sum of sixteen terms. Each term is unique in the powers of coordinates used to evaluate the dipole moment matrix elements. Many of these terms can be neglected because their delta-functions force them to equal zero. Also, examination of Equation 8.29 suggests that, in order to contribute to the third-order response function, a time-domain term must have a nonzero derivative with respect to $t_1$. Even though Equation 8.29 assumes the classical limit, the neglected higher order terms would involve higher order $t_1$ derivatives.

9.3 Expansion of the Dipole Moment Matrix Operators

As demonstrated earlier, frequency-domain TCF $A(\omega_1, \omega_2, \omega_3)$ is written below.

$$ A(\omega_1, \omega_2, \omega_3) = \sum_{abcd} \mu_{ad}^i \mu_{dc}^j \mu_{cb}^k \mu_{ba}^\ell \delta(\omega_1 - E_{ab}/\hbar)\delta(\omega_2 - E_{ac}/\hbar)\delta(\omega_3 - E_{ad}/\hbar) $$

(9.4)

The four dipole moment matrix elements $\mu_{ad}^i$, $\mu_{dc}^j$, $\mu_{cd}^k$, and $\mu_{ba}^\ell$ are expanded according to Equation 9.3, yielding a sum of sixteen distinct terms. Several of the terms
that arise from this expansion can clearly be eliminated. The terms $A_{0001}$, $A_{0010}$, $A_{0100}$, $A_{1000}$, written in terms of one $\mu'$ and three $\mu^0$, as well as $A_{1110}$, $A_{1101}$, $A_{1011}$, and $A_{0111}$, in terms of three $\mu'$ and one $\mu^0$ come out to zero when the delta functions built into the dipole moment matrix elements are enforced. The delta functions give nonzero values to the eight remaining terms. However, seven of these nonzero terms can also be eliminated.

The first of these terms is $A_{0000}$, which is written:

$$A_{0000}(\omega_1, \omega_2, \omega_3) = \frac{1}{Q} \mu_i^0 \mu_j^0 \mu_k^0 \mu_\ell^0 \sum_a e^{-\beta E_a} \delta(\omega_1) \delta(\omega_2) \delta(\omega_3)$$

(9.5)

The sum over index $a$ is a sum over all possible states $a$, and is therefore considered an infinite sum. It takes on the same value as the partition function $Q$.

$$\sum_{a=0}^{\infty} e^{-\beta E_a} = e^{-\beta \hbar \Omega/2} \sum_{a=0}^{\infty} e^{-\beta E_a} = \frac{e^{-\beta \hbar \Omega/2}}{1 - e^{-\beta \hbar \Omega}} = Q$$

(9.6)

After evaluating the sum, enforcing the delta functions, and back Fourier transforming the result, $A_{0000}$ is found to be the product of four $\mu^0$ elements. This term is eliminated from the third-order response function since its derivative with respect to $t_1$ is zero.

$$A_{0000}(t_1, t_2, t_3) = \mu_i^0 \mu_j^0 \mu_k^0 \mu_\ell^0$$

(9.7)

The next six nonzero terms contain two $\mu^0$ and two $\mu'$ matrix elements. All of the terms are evaluated the same way, by enforcing the delta functions and assessing the
value of the infinite sums over index $a$. The results are shown in the time domain. Three of these terms do not contribute to $R^{(3)}$ because their derivatives with respect to $t_1$ are also zero.

\[
A^{0110}(t_1, t_2, t_3) = \mu_i^0 \mu_j^0 \mu_k^0 \mu_\ell^0 \left( \frac{\hbar}{2m\Omega} \right) \left( \frac{1}{1 - e^{-\beta\hbar\Omega}} \right) [e^{-\beta\hbar\Omega} e^{i\Omega t_2} + e^{-i\Omega t_2}]
\]

\[
A^{1100}(t_1, t_2, t_3) = \mu_i^0 \mu_j^0 \mu_k^0 \mu_\ell^0 \left( \frac{\hbar}{2m\Omega} \right) \left( \frac{1}{1 - e^{-\beta\hbar\Omega}} \right) [e^{-\beta\hbar\Omega} e^{i\Omega t_3} + e^{-i\Omega t_3}]
\]

\[
A^{1010}(t_1, t_2, t_3) = \mu_i^0 \mu_j^0 \mu_k^0 \mu_\ell^0 \left( \frac{\hbar}{2m\Omega} \right) \left( \frac{1}{1 - e^{-\beta\hbar\Omega}} \right) [e^{-\beta\hbar\Omega} e^{i\Omega(t_2 + t_3)} + e^{-i\Omega(t_2 + t_3)}] \quad (9.8)
\]

The remaining three terms appear to contribute to $R^{(3)}$ because their delta functions give them nonzero values and they also possess nonzero $t_1$ derivatives.

\[
A^{0011}(t_1, t_2, t_3) = \mu_i^0 \mu_j^0 \mu_k^0 \mu_\ell^0 \left( \frac{\hbar}{2m\Omega} \right) \left( \frac{1}{1 - e^{-\beta\hbar\Omega}} \right) [e^{-\beta\hbar\Omega} e^{i\Omega t_1} + e^{-i\Omega t_1}]
\]

\[
A^{0101}(t_1, t_2, t_3) = \mu_i^0 \mu_j^0 \mu_k^0 \mu_\ell^0 \left( \frac{\hbar}{2m\Omega} \right) \left( \frac{1}{1 - e^{-\beta\hbar\Omega}} \right) [e^{-\beta\hbar\Omega} e^{i\Omega(t_1 + t_2)} + e^{-i\Omega(t_1 + t_2)}]
\]

\[
A^{1001}(t_1, t_2, t_3) = \mu_i^0 \mu_j^0 \mu_k^0 \mu_\ell^0 \left( \frac{\hbar}{2m\Omega} \right) \left( \frac{1}{1 - e^{-\beta\hbar\Omega}} \right) [e^{-\beta\hbar\Omega} e^{i\Omega(t_1 + t_2 + t_3)} + e^{-i\Omega(t_1 + t_2 + t_3)}] \quad (9.9)
\]

The final nonzero term in TCF $A$ is $A^{1111}$, in which all the dipole matrix elements appear as $\mu'$. For ease of manipulation, $A^{1111}$ is split into a sum of six distinct terms, indexed $a$ through $f$.

\[
A^{1111a}(t_1, t_2, t_3) = \mu_i^0 \mu_j^0 \mu_k^0 \mu_\ell^0 \left( \frac{\hbar}{2m\Omega} \right)^2 \left( \frac{1}{1 - e^{-\beta\hbar\Omega}} \right)^2 [e^{-2\beta\hbar\Omega} e^{i\Omega(t_1 + 2t_2 + t_3)} + e^{-i\Omega(t_1 + 2t_2 + t_3)}]
\]

\[
A^{1111b}(t_1, t_2, t_3) = \mu_i^0 \mu_j^0 \mu_k^0 \mu_\ell^0 \left( \frac{\hbar}{2m\Omega} \right)^2 \left( \frac{1}{1 - e^{-\beta\hbar\Omega}} \right)^2 [e^{-2\beta\hbar\Omega} e^{i\Omega(t_1 + 2t_2 + t_3)} + e^{-i\Omega(t_1 + 2t_2 + t_3)}]
\]

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\begin{align*}
A_{111}^{111c}(t_1, t_2, t_3) &= \mu_i' \mu_j' \mu_k' \mu_\ell' \left( \frac{\hbar}{2m\Omega} \right)^2 \left( \frac{1}{1 - e^{-\beta\hbar\Omega}} \right)^2 (e^{-\beta\hbar\Omega} + e^{-2\beta\hbar\Omega}) e^{i\Omega(t_1 + t_3)} \\
A_{111}^{111d}(t_1, t_2, t_3) &= \mu_i' \mu_j' \mu_k' \mu_\ell' \left( \frac{\hbar}{2m\Omega} \right)^2 \left( \frac{1}{1 - e^{-\beta\hbar\Omega}} \right)^2 (1 + e^{-\beta\hbar\Omega}) e^{-i\Omega(t_1 + t_3 + 3)} \\
A_{111}^{111e}(t_1, t_2, t_3) &= \mu_i' \mu_j' \mu_k' \mu_\ell' \left( \frac{\hbar}{2m\Omega} \right)^2 \left( \frac{1}{1 - e^{-\beta\hbar\Omega}} \right)^2 2e^{-\beta\hbar\Omega} e^{i\Omega(t_3 - t_1)} \\
A_{111}^{111f}(t_1, t_2, t_3) &= \mu_i' \mu_j' \mu_k' \mu_\ell' \left( \frac{\hbar}{2m\Omega} \right)^2 \left( \frac{1}{1 - e^{-\beta\hbar\Omega}} \right)^2 2e^{-\beta\hbar\Omega} e^{-i\Omega(t_3 - t_1)} \quad (9.10)
\end{align*}

Note that in the frequency domain, the exponentials of the form $e^{i\Omega t}$ become delta functions of the form $\delta(\omega - \Omega)$. This property of the frequency-domain 1111 terms will prove useful in deriving a general relationship between TCFs $A$ and $B$.

Similar analysis is performed for TCF $B(\omega_1, \omega_2, \omega_3)$. Enforcing the delta functions eliminates eight terms, and the $B^{0000}$, $B^{0110}$, $B^{1100}$, and $B^{1010}$ terms are found to have zero $t_1$ derivatives. The terms $B^{0011}$, $B^{0101}$, and $B^{1001}$ terms are identical to the ones for TCF $A$. Since the $R^{(3)}$ expression, as shown in Equation 8.24, is written in terms of differences between TCFs $A$ and $B$, the common terms between the TCFs cancel out to zero and do not need to be considered.

The only nonzero term remaining for TCF $B$ is the $B^{1111}$ term, which is also written as a sum of six terms, indexed $a$ through $f$. Note that the $B^{1111a}$ and $B^{1111b}$ terms are identical to those found for TCF $a$, while terms $B^{1111c}$ through $B^{1111d}$ are unique.

\begin{align*}
B_{111}^{111a}(t_1, t_2, t_3) &= \mu_i' \mu_j' \mu_k' \mu_\ell' \left( \frac{\hbar}{2m\Omega} \right)^2 \left( \frac{1}{1 - e^{-\beta\hbar\Omega}} \right)^2 2e^{-2\beta\hbar\Omega} e^{i\Omega(t_1 + 2t_2 + t_3)} \\
B_{111}^{111b}(t_1, t_2, t_3) &= \mu_i' \mu_j' \mu_k' \mu_\ell' \left( \frac{\hbar}{2m\Omega} \right)^2 \left( \frac{1}{1 - e^{-\beta\hbar\Omega}} \right)^2 2e^{-\beta\hbar\Omega} e^{i\Omega(t_1 + 2t_2 + t_3)}
\end{align*}
\begin{align*}
B_{1111c}(t_1, t_2, t_3) &= \mu_i' \mu_j' \mu_k' \mu_{\ell}' \left( \frac{\hbar}{2m\Omega} \right)^2 \left( \frac{1}{1 - e^{-\beta\hbar\Omega}} \right)^2 e^{-\beta\hbar\Omega} e^{i\Omega(t_1 + t_3)} \\
B_{1111d}(t_1, t_2, t_3) &= \mu_i' \mu_j' \mu_k' \mu_{\ell}' \left( \frac{\hbar}{2m\Omega} \right)^2 \left( \frac{1}{1 - e^{-\beta\hbar\Omega}} \right)^2 e^{-\beta\hbar\Omega} e^{-i\Omega(t_1 + t_3)} \\
B_{1111e}(t_1, t_2, t_3) &= \mu_i' \mu_j' \mu_k' \mu_{\ell}' \left( \frac{\hbar}{2m\Omega} \right)^2 \left( \frac{1}{1 - e^{-\beta\hbar\Omega}} \right)^2 (e^{-\beta\hbar\Omega} + 1)e^{i\Omega(t_3 - t_1)} \\
B_{1111f}(t_1, t_2, t_3) &= \mu_i' \mu_j' \mu_k' \mu_{\ell}' \left( \frac{\hbar}{2m\Omega} \right)^2 \left( \frac{1}{1 - e^{-\beta\hbar\Omega}} \right)^2 (e^{-2\beta\hbar\Omega} + e^{-\beta\hbar\Omega})e^{-i\Omega(t_3 - t_1)} \quad (9.11)
\end{align*}

Considering only the $A_{1111}$ and $B_{1111}$ terms, it is now possible to define an exact relationship between the two TCFs and use it to further simplify $R^{(3)}$.

### 9.4 Frequency-Domain Relationship between TCFs A and B

To discern a relationship between TCFs $A(\omega_1, \omega_2, \omega_3)$ and $B(\omega_1, \omega_2, \omega_3)$, it is helpful to examine how the six individual 1111 terms of the two TCFs are related.

\begin{align*}
A_{1111a} &= B_{1111a} \\
A_{1111b} &= B_{1111b} \\
A_{1111c} &= \frac{1}{2} (1 + e^{-\beta\hbar\Omega}) B_{1111c} \\
A_{1111d} &= \frac{1}{2} (1 + e^{\beta\hbar\Omega}) B_{1111d} \\
A_{1111e} &= \left( \frac{2}{1 + e^{\beta\hbar\Omega}} \right) B_{1111e} \\
A_{1111f} &= \left( \frac{2}{1 + e^{-\beta\hbar\Omega}} \right) B_{1111f}
\end{align*}

Using this information, the a general relationship, indicated by the frequency-domain function $g(\omega_1, \omega_2, \omega_3)$, between $A(\omega_1, \omega_2, \omega_3)$ and $B(\omega_1, \omega_2, \omega_3)$ is derived.
Table 9.1: The values that frequencies $\omega_1$, $\omega_2$, and $\omega_3$ take on as dictated by the delta functions of the six 1111 terms of the TCFs A and B

<table>
<thead>
<tr>
<th>Term</th>
<th>$\omega_1$</th>
<th>$\omega_2$</th>
<th>$\omega_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>$\Omega$</td>
<td>$2\Omega$</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>b</td>
<td>$-\Omega$</td>
<td>$-2\Omega$</td>
<td>$-\Omega$</td>
</tr>
<tr>
<td>c</td>
<td>$\Omega$</td>
<td>0</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>d</td>
<td>$-\Omega$</td>
<td>0</td>
<td>$-\Omega$</td>
</tr>
<tr>
<td>e</td>
<td>$-\Omega$</td>
<td>0</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>f</td>
<td>$\Omega$</td>
<td>0</td>
<td>$-\Omega$</td>
</tr>
</tbody>
</table>

This relationship can also be applied to the TCFs in negative frequency. This is accomplished by replacing all the $\omega_\alpha$ by $-\omega_\alpha$.

$$A(\omega_1, \omega_2, \omega_3) = g(\omega_1, \omega_2, \omega_3) B(\omega_1, \omega_2, \omega_3)$$

$$g(\omega_1, \omega_2, \omega_3) = \frac{1 + e^{-\beta h(\omega_1 + \omega_3 - \omega_2)/2}}{1 + e^{-\beta h(\omega_1 - \omega_3)/2}} \tag{9.12}$$

$$A(-\omega_1, -\omega_2, -\omega_3) = g(-\omega_1, -\omega_2, -\omega_3) B(-\omega_1, -\omega_2, -\omega_3)$$

$$g(-\omega_1, -\omega_2, -\omega_3) = \frac{1 + e^{-\beta h(\omega_2 - \omega_1 - \omega_3)/2}}{1 + e^{-\beta h(\omega_3 - \omega_1)/2}} \tag{9.13}$$
Making use of Equations 9.12 and 9.13, the frequency-domain $R^{(3)}$ expression can now be written in terms of $B(\omega_1, \omega_2, \omega_3)$ alone.

$$R^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{i}{\hbar^3} \tanh(\beta \hbar \omega_1 / 2) \left[ (1 + e^{\beta \hbar \omega_1}) (1 - g(\omega_1, \omega_2, \omega_3) B(\omega_1, \omega_2, \omega_3) +
(1 + e^{-\beta \hbar \omega_1}) (1 - g(-\omega_1, -\omega_2, -\omega_3) B(-\omega_1, -\omega_2, -\omega_3) \right]$$

9.5 Eliminating the Imaginary Part of TCF $B$

Next, consider the classical limit of the simplified $R^{(3)}$ expression. Two of the three $\hbar$ prefactors have been eliminated completely from the expression and $R^{(3)}$ is written in terms of $B_R(\omega_1, \omega_2, \omega_3)$ and $B_I(\omega_1, \omega_2, \omega_3)$.

$$R^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{i}{\hbar^3} \left( \frac{\beta \hbar \omega_1}{2} \right) \left[ \frac{\beta \hbar}{4} (2 \omega_3 - \omega_2) \right] \times
2 \left[ \beta \hbar \omega_1 B_R(\omega_1, \omega_2, \omega_3) + 4 B_I(\omega_1, \omega_2, \omega_3) \right]$$

(9.14)

In this limit, $B_R(\omega_1, \omega_2, \omega_3)$ is equivalent to the classical time correlation function that can be calculated using molecular dynamics methods. Finding a general relationship between $B_R(\omega_1, \omega_2, \omega_3)$ and $B_I(\omega_1, \omega_2, \omega_3)$ will allow the final $\hbar$ prefactor to be removed and give an expression solely in terms of $B_R(\omega_1, \omega_2, \omega_3)$ that is valid for all frequencies.

A one-time correlation function $f(t)$ has a simple function relationship of the form $f_R(\omega) = \tanh(\beta \hbar \omega / 2) f_I(\omega)$ between the Fourier transforms of its real and imaginary parts.
A relationship of this nature between $B_R(\omega_1, \omega_2, \omega_3)$ and $B_I(\omega_1, \omega_2, \omega_3)$ is not immediately obvious. To attempt to find one, each term of $B(t_1, t_2, t_3)$ contributing to the third-order response, namely $B^{1111}$, was separated into its real and imaginary parts, and the two parts were Fourier transformed separately. For each term, the ratio between $B_R(\omega_1, \omega_2, \omega_3)$ and $B_I(\omega_1, \omega_2, \omega_3)$ was determined. In this analysis, the $B^{1111}$ terms were grouped as $B^{1111ab} = B^{1111a} + B^{1111b}$, $B^{1111cd} = B^{1111c} + B^{1111d}$, and $B^{1111ef} = B^{1111e} + B^{1111f}$.

\begin{equation}
B^{1111ab}(\omega_1, \omega_2, \omega_3) = -\tanh[\beta h(\omega_1 + \omega_2 + \omega_3)/4]B^{1111ab}_R(\omega_1, \omega_2, \omega_3) \tag{9.15}
\end{equation}

\begin{equation}
B^{1111cd}_I(\omega_1, \omega_2, \omega_3) = 0 \times B^{1111cd}_R(\omega_1, \omega_2 + \omega_3) \tag{9.15}
\end{equation}

\begin{equation}
B^{1111ef}_I(\omega_1, \omega_2, \omega_3) = -\tanh[\beta h(\omega_1 - \omega_3)/4]B^{1111ef}_R(\omega_1, \omega_2, \omega_3) \tag{9.16}
\end{equation}

Comparison of the three results led to the derivation of a general relationship between $B_R(\omega_1, \omega_2, \omega_3)$ and $B_I(\omega_1, \omega_2, \omega_3)$. The general relationship takes into account the values in terms of $\Omega$ that the frequencies $\omega_1$, $\omega_2$, and $\omega_3$ take on based on each term’s delta functions.

\begin{equation}
B_I(\omega_1, \omega_2, \omega_3) = -\tanh\left[\frac{\beta h(\omega_1 + 2\omega_2 - \omega_3)}{4}\right]B_R(\omega_1, \omega_2, \omega_3) \tag{9.17}
\end{equation}

Equation 9.17 is exact for the harmonic system. With this relationship, it is straightforward to make one final simplification to the $R^{(3)}$ expression, which removes the final factor of $h$ in the classical limit expression.
9.6 The Final $R^{(3)}$ Expression

In the classical limit, the third-order response function can now be written as

\[ B_R(\omega_1, \omega_2, \omega_3) \] multiplied by a set of frequency factors. Applying the classical limit of Equation 9.17 to Equation 9.14 gives the following result.

\[
R^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{i}{\hbar^3} \left( \frac{\beta \hbar \omega_1}{2} \right) \left[ \frac{\beta \hbar}{4} (2\omega_3 - \omega_2) \right] \times 
\left[ 2\beta \hbar \omega_1 - \beta \hbar (\omega_1 + 2\omega_2 - \omega_3) \right] B_R(\omega_1, \omega_2, \omega_3)
\]

\[
R^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{i\beta^3}{8} \left( 2\omega_1^2 \omega_3 - \omega_1^2 \omega_2 - 5\omega_1 \omega_2 \omega_3 + 2\omega_1 \omega_2^2 + 2\omega_1 \omega_3^2 + 2\omega_1 \omega_2 \omega_3 \right) \times 
B_R(\omega_1, \omega_2, \omega_3) \quad (9.18)
\]

Taking time derivatives of the back Fourier transform of $B_R(\omega_1, \omega_2, \omega_3)$ allow this expression to be rewritten in the time domain.

\[
R^{(3)}(t_1, t_2, t_3) = \frac{\beta^3}{8} \left( \frac{d^3}{dt_1^2 dt_2^2} - 2\frac{d^3}{dt_1 dt_2^2} - 2\frac{d^3}{dt_1^2 dt_3^2} - 2\frac{d^3}{dt_1 dt_2 dt_3^2} + 5\frac{d^3}{dt_1 dt_2 dt_3} \right) \times 
B_R(t_1, t_2, t_3) \quad (9.19)
\]

To examine high-frequency dynamics, taking the classical limit of the $R^{(3)}$ expression is not realistic. The third-order response function is written without taking the classical limit as follows:

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\[ R^{(3)}(\omega_1, \omega_2, \omega_3) = \left( \frac{i}{\hbar^3} \right) \tanh(\beta \hbar \omega_1/2) \times \]

\[ \{ (1 + e^{\beta \hbar \omega_1})[1 - f(\omega_1, \omega_2, \omega_3)](1 - \tanh[\beta \hbar(\omega_1 + 2\omega_2 - \omega_3)/4]) + \]

\[ (1 + e^{-\beta \hbar \omega_1})[1 - f(-\omega_1, -\omega_2, -\omega_3)](1 + \tanh[\beta \hbar(\omega_1 + 2\omega_2 - \omega_3)/4]) \} \times \]

\[ B_R(\omega_1, \omega_2, \omega_3) \quad (9.20) \]

Equation 9.20 represents the third-order response function in a form that can be evaluated using classical MD and TCF computational techniques. In calculating \( R^{(3)} \), the time domain TCF \( B_R(t_1, t_2, t_3) \) is calculated as its classical counterpart \( \langle \mu_j(t_2 + t_1)\mu_i(t_3 + t_2 + t_1)\mu_k(t_1)\mu_\ell(0) \rangle \) and Fourier transformed into the frequency domain. It may then be multiplied by the necessary frequency factors then back transformed to obtain \( R^{(3)}(t_1, t_2, t_3) \). The resulting response function may then applied to Equation 8.1 to obtain a 2D-IR signal.

9.7 Limitation of the Harmonic Approximation

It is well-established knowledge that a harmonic oscillator model system with a linearly varying dipole yields zero signal in a 2D-IR experiment. The theory presented under the harmonic approximation thus serves as a means of filtering harmonic dynamics out of simulation results and highlighting anharmonic couplings.

It is simple to prove that \( R^{(3)} = 0 \) under these conditions using Poisson brackets, which are classically equivalent to commutators. For two functions \( u \) and \( v \) of the variables \( p \) (momentum) and \( q \) (position),
\[ \{u,v\}_{q,p} = \frac{du}{dq_i} \frac{dv}{dp_i} - \frac{du}{dp_i} \frac{dv}{dq_i} \]  
(9.21)

For a harmonic system, the following two expressions are used to describe the position \( q \) and dipole \( \mu \).

\[
q(t) = q(0)f(t) + v(0)g(t)
\]

\[
\mu = \mu_0 + \mu'q
\]  
(9.22)

To prove that \( R^{(3)} = 0 \) under these conditions, the leftmost Poisson bracket in the \( R^{(3)} \) expression, between \( \mu_i(t_3 + t_2 + t_1) \) and \( \mu_j(t_2 + t_1) \), is evaluated first, taking into account the information provided in Equation 9.22.

\[
\begin{align*}
\mu_i(t_1, t_2, t_3) &= \mu_0 + \mu'[q(0)f(t_1 + t_2 + t_3) + v(0)g(t_1 + t_2 + t_3)] \\
\frac{d\mu_i}{dq} &= \mu'f(t_1 + t_2 + t_3) \\
\frac{d\mu_i}{dv} &= \mu'g(t_1 + t_2 + t_3)
\end{align*}
\]

\[
\begin{align*}
\mu_j(t_2 + t_1) &= \mu_0 + \mu'[q(0)f(t_1 + t_2) + v(0)g(t_1 + t_2)] \\
\frac{d\mu_j}{dq} &= \mu'f(t_1 + t_2) \\
\frac{d\mu_j}{dv} &= \mu'g(t_1 + t_2)
\end{align*}
\]  
(9.23)

The Poisson bracket comes out to

\[
\begin{align*}
\{\mu_i(t_3 + t_2 + t_1), \mu_j(t_1 + t_2)\} &= \mu'^2[f(t_1 + t_2 + t_3)g(t_1 + t_2) - \\
& \quad f(t_1 + t_2)g(t_1 + t_2 + t_3)]
\end{align*}
\]  
(9.24)
This result has no velocity or position dependence, so taking the next Poisson bracket will give derivatives of zero, making the entire $R^{(3)}$ expression zero.

It is interesting to consider exactly how the harmonic theory of 2D-IR leads to zero signal. The individual TCFs $A$ and $B$ are individually nonzero under this approximation. Thus, either the relationship $g$ between then or the tanh relationship between $B_R$ and $B_I$ causes the expression to rigorously equal zero.

Beginning with Equation 8.24, it is possible to use all the 1111 terms of TCFs $A$ and $B$, the terms that contribute to the $R^{(3)}$ expression, to determine the differences $B(\omega_1, \omega_2, \omega_3) - A(\omega_1, \omega_2, \omega_3)$ and $B(-\omega_1, -\omega_2, -\omega_3) - A(-\omega_1, -\omega_2, -\omega_3)$.

\[
B(\omega_1, \omega_2, \omega_3) - A(\omega_1, \omega_2, \omega_3) = B^{111e} - A^{111e} + B^{111d} - A^{111d} + B^{111e} - A^{111e} + B^{111f} - A^{111f}
\]

\[
B(\omega_1, \omega_2, \omega_3) = Ke^{-\beta\hbar\Omega} \delta(\omega_1 - \Omega)\delta(\omega_3 - \Omega) - \delta(\omega_1 + \Omega)\delta(\omega_3 + \Omega) + \delta(\omega_1 + \Omega)\delta(\omega_3 - \Omega) - \delta(\omega_1 - \Omega)\delta(\omega_3 + \Omega)
\]

\[
K = \mu_i^j\mu_k^l\mu_{k'}^l\left(\frac{\hbar}{2m\Omega}\right)\left(\frac{1}{1 - e^{-\beta\hbar\Omega}}\right)
\]

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\[ R^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{i}{\hbar^3} \left( \frac{\beta \hbar \omega_1}{2} \right) \mu_i' \mu_j' \mu_k' \mu_\ell' \left( \frac{\hbar}{2m\Omega} \right) \left( \frac{1}{1 - e^{-\beta \hbar \Omega}} \right) \times \]

\[
\left( e^{-\beta \hbar \Omega} + e^{\beta \hbar \Omega} e^{-\beta \hbar \Omega} - 1 - e^{-\beta \hbar \Omega} \right) \delta(\omega_1 - \Omega) \delta(\omega_3 - \Omega) +
\]

\[
(-1 - e^{-\beta \hbar \Omega} + e^{-\beta \hbar \Omega} e^{-\beta \hbar \Omega}) \delta(\omega_1 + \Omega) \delta(\omega_3 + \Omega) +
\]

\[
(1 + e^{\beta \hbar \Omega} - e^{-\beta \hbar \Omega} - e^{-\beta \hbar \Omega} e^{-\beta \hbar \Omega}) \delta(\omega_1 + \Omega) \delta(\omega_3 - \Omega) +
\]

\[
(1 + e^{-\beta \hbar \Omega} - e^{\beta \hbar \Omega} - e^{-\beta \hbar \Omega} e^{-\beta \hbar \Omega}) \delta(\omega_1 + \Omega) \delta(\omega_3 + \Omega)
\]

(9.26)

In developing this theory of 2D-IR spectroscopy, it is useful to find the lowest order reference system that will give a signal. This reference system is clearly not the harmonic oscillator, as demonstrated in this chapter.
Chapter 10

TCF Theory: 2D-IR Spectroscopy (Anharmonic Approximation)

As previously stated, the third-order response function for two-dimensional infrared spectroscopy gives no signal with a reference system of a harmonic oscillator and linearly varying dipole. To obtain a non-zero signal, the reference system of an anharmonic oscillator, also with a linearly varying dipole, is examined. The anharmonicity is built into the theory by using a cubic perturbation of the form $\lambda q^3$ to the harmonic potential. Anharmonic states are represented as a superposition of harmonic states. The result of this development is a different expression for the third-order response function which does give a 2D-IR signal.

10.1 The Anharmonic Approximation with Linearly Varying Dipole

One way to represent an anharmonic oscillator is through the use of the Morse potential, but this method would require the anharmonic states to be defined in terms of complicated Bessel functions. For the sake of simplicity, the anharmonic approximation was invoked by applying a cubic perturbation to the harmonic potential shown in Equation 9.1.
\[ V = m\Omega^2q^2/2 + \lambda q^3 \] (10.1)

The constant \( \lambda \) indicates the degree of anharmonicity or the strength of the perturbation. According to first-order perturbation theory, the anharmonic states can be represented as sums of harmonic states.

\[
|i\rangle_{ANH} = |i\rangle_{HARM} + \sum_{i\neq k}^{\alpha} \frac{\langle k|\lambda q^3|i\rangle}{E_i - E_k} |k\rangle
\] (10.2)

Note that Equation 10.2 is valid only for small perturbations, \( \text{i.e.} \ \frac{\lambda^2 \hbar}{m^3 \omega^5} >> 1 \). The matrix elements \( \langle k|q^3|i\rangle \) are nonzero in only a few cases: \( k = i + 1, k = i - 1, k = i + 3, \) and \( k = i - 3 \). Each anharmonic state is completely described, within this approximation, as a superposition of five harmonic states weighted by constants.

\[
|i\rangle_{anh} = |i\rangle_{harm} + c_{(i+1)}\lambda|i + 1\rangle + c_{(i-1)}\lambda|i - 1\rangle + c_{(i+3)}\lambda|i + 3\rangle + c_{(i-3)}|i - 3\rangle
\] (10.3)

The perturbation constants can easily be derived by solving for the matrix element in Equation 10.2. The constants give zero results for transitions to negative states such as \( i = -1 \). In the harmonic limit, all perturbation constants go to one.

\[
c_{(i+)} = \frac{-b(i + 1)^{3/2}}{\Omega^{5/2}}
\]
\[
c_{(i-)} = \frac{b i^{3/2}}{\Omega^{5/2}}
\]
$$c_{(i+3)} = \frac{-b\sqrt{(i + 1)(i + 2)(i + 3)}}{9\Omega^{5/2}}$$

$$c_{(i-3)} = \frac{b\sqrt{i(i - 1)(i - 2)}}{9\Omega^{5/2}}$$

$$b = \sqrt{\frac{9h}{8m^3}} \quad \Omega = (E_{i+1} - E_i)/\hbar$$

(10.4)

In Table 10.1, several constants composed of sums of $c_{i+}$ and $c_{1-}$ are defined for convenience in writing out expressions for TCFs $A$ and $B$ later in the chapter.
10.2 Simplifying the Approximation

Since the time correlation functions that result from expansion of the third-order response function’s commutators can be analytically related to TCFs $A$ and $B$, the function of the anharmonic approximation, as with the harmonic, is to determine a relationship between TCFs $A$ and $B$, then $B_R$ and $B_I$ with the end result of calculating $R^{(3)}$ as $B_R$ multiplied by a set of frequency factors.

\[
A(\omega_1, \omega_2, \omega_3) = \frac{1}{Q} \sum_{ABCD}^{\infty} e^{-\beta E_A} \mu_{AD}^i \mu_{DC}^j \mu_{CB}^k \mu_{BA}^\ell \times
\delta(\omega_1 - E_{AB}/\hbar) \delta(\omega_2 - E_{AC}/\hbar) \delta(\omega_3 - E_{AD}/\hbar)
\]

\[
B(\omega_1, \omega_2, \omega_3) = \frac{1}{Q} \sum_{ABCD}^{\infty} e^{-\beta E_A} \mu_{DC}^i \mu_{AD}^j \mu_{CB}^k \mu_{BA}^\ell \times
\delta(\omega_1 - E_{AB}/\hbar) \delta(\omega_2 - E_{AC}/\hbar) \delta(\omega_3 - E_{DC}/\hbar)
\]  

(10.5)

In Equation 10.5, the indices $A$, $B$, $C$, and $D$ now represent anharmonic states. In TCFs $A$ and $B$ the dipole matrix elements are expanded out to first order, i.e. $\langle \alpha | \mu | \beta \rangle = \mu_0 + \mu' \langle \alpha | q | \beta \rangle$. States $\alpha$ and $\beta$ are now anharmonic states, each one is a sum of five harmonic states weighted by constants. Consequently, the final result is that for each TCF, the infinite sum of $25^4$ terms must be evaluated. It is obvious that simplification is required to make the application of this approximation feasible.

One realistic simplification is assume that anharmonic state $|A\rangle$ will be ground-state dominated, as indicated by the Boltzmann factor in both TCFs. Formally, this idea is represented in the theory by assuming that the $i + 3$ and $i - 3$ transitions make
negligible contributions, and therefore may be neglected. Restriction of state $|A\rangle$ in turn restricts the values that states $|B\rangle$, $|C\rangle$, and $|D\rangle$ can assume, since only $\langle n|\mu|n, n \pm 1 \rangle$ matrix elements are nonzero. Anharmonic state $a$ is restricted as a sum from zero to one. Consequently, the sums in Equation 10.5 are restricted as shown.

$$A(\omega_1, \omega_2, \omega_3) = \frac{1}{Q} \sum_{A=0}^{1} \sum_{D=0}^{2} \sum_{B=0}^{2} \sum_{C=0}^{3} e^{-\beta E_A} \mu_i^A \mu_j^D \mu_k^C \mu_\ell^B \times$$

$$\delta(\omega_1 - E_{AB}/\hbar) \delta(\omega_2 - E_{AC}/\hbar) \delta(\omega_3 - E_{AD}/\hbar)$$

$$B(\omega_1, \omega_2, \omega_3) = \frac{1}{Q} \sum_{A=0}^{1} \sum_{D=0}^{2} \sum_{B=0}^{2} \sum_{C=0}^{3} e^{-\beta E_A} \mu_i^D \mu_j^A \mu_k^C \mu_\ell^B \times$$

$$\delta(\omega_1 - E_{AB}/\hbar) \delta(\omega_2 - E_{AC}/\hbar) \delta(\omega_3 - E_{DC}/\hbar)$$

(10.6)

Additional simplifications can be made by decomposing the sums over anharmonic states into sums over harmonic states. As a result, the sums that make up TCFs $A$ and $B$ become a sum of three harmonic sums, each corresponding to a harmonic state $a = 0$, 1, or 2, as shown below.

$$\sum_{A=0}^{1} \sum_{D=0}^{2} \sum_{B=0}^{2} \sum_{C=0}^{3} = \sum_{a=0}^{1} \sum_{d=0}^{2} \sum_{b=0}^{2} \sum_{c=0}^{3} + \sum_{a=1}^{2} \sum_{d=0}^{2} \sum_{b=0}^{2} \sum_{c=0}^{3} + \sum_{a=2}^{2} \sum_{d=1}^{3} \sum_{b=1}^{3} \sum_{c=0}^{4}$$

(10.7)

The resulting sums can be decomposed even further by eliminating terms that give zero as a result of improper overlap of states. After these simplifications have been made, only forty-five terms contribute to each TCF. Expanding the sums and evaluating each one with a linearly varying dipole simplifies the TCFs even further down to sums
of thirteen nonzero terms. This procedure is the same for both TCFs $A$ and $B$. Tables 10.2 and 10.3 display all the terms contributing to TCFs $A$ and $B$. A term is written out as follows:

$$
\left( \frac{\hbar}{2m\Omega} \right) (1 - e^{-\beta\Omega}) \mu_i' \mu_j' \mu_k' \mu_l' K \delta
$$

(10.8)

$K$ indicates the combination of perturbation constants included in the term. These constants are the same for TCFs $A$ and $B$. $\delta$ indicates the term’s delta functions, which are typically different for TCFs $A$ and $B$.

10.3 Relating the Anharmonic TCFs $A$ and $B$

In Chapter 9’s analysis involving the harmonic approximation, TCFs $A$ and $B$ were related by taking ratios between terms with identical delta functions and using the results to generalize the relationship. In the anharmonic approximation, there is no obvious means of determining such a relationship. Instead, all possible harmonic transitions appearing in the anharmonic terms of TCFs $A$ and $B$ are considered. The analysis is summarized in Table 10.4. For simplicity, the perturbation constants are not included in the analysis. First, a general formula is developed for the harmonic case, then the perturbation constants will be re-incorporated into the expression.

Next, the prefactors for TCFs $A$ and $B$ are compared in terms that have the same sets of delta functions. When $i < 2$, some of the coefficients go to zero. Heavyside step functions of the form $\theta(\omega)$ are imposed to deal with cases when $i = 0$. In these cases,
<table>
<thead>
<tr>
<th>Indices (ADBC)</th>
<th>K</th>
<th>( \delta ) (TCF A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0110</td>
<td>( k_1^2 k_2^2 )</td>
<td>( \delta(\omega_1 + \Omega)\delta(\omega_2)\delta(\omega_3 + \Omega) )</td>
</tr>
<tr>
<td>0121</td>
<td>( 2k_1 k_2^2 k_3 )</td>
<td>( \delta(\omega_1 + \Omega)\delta(\omega_2 + 2\Omega)\delta(\omega_3 + \Omega) )</td>
</tr>
<tr>
<td>1001</td>
<td>( k_0 k_1^2 k_2 )</td>
<td>( \delta(\omega_1 - \Omega)\delta(\omega_2)\delta(\omega_3 - \Omega) )</td>
</tr>
<tr>
<td>1021</td>
<td>( 2k_0 k_1 k_2 k_3 )</td>
<td>( \delta(\omega_1 + \Omega)\delta(\omega_2)\delta(\omega_3 - \Omega) )</td>
</tr>
<tr>
<td>1201</td>
<td>( 2k_0 k_1 k_2 k_3 )</td>
<td>( \delta(\omega_1 - \Omega)\delta(\omega_2)\delta(\omega_3 + \Omega) )</td>
</tr>
<tr>
<td>1212</td>
<td>( 4k_0 k_1^2 k_3^2 )</td>
<td>( \delta(\omega_1 + \Omega)\delta(\omega_2)\delta(\omega_3 + \Omega) )</td>
</tr>
<tr>
<td>1232</td>
<td>( 6k_0 k_2^2 k_3 )</td>
<td>( \delta(\omega_1 + \Omega)\delta(\omega_2 + 2\Omega)\delta(\omega_3 + \Omega) )</td>
</tr>
<tr>
<td>2110</td>
<td>( 2kk_1 k_2^2 )</td>
<td>( \delta(\omega_1 - \Omega)\delta(\omega_2 - 2\Omega)\delta(\omega_3 - \Omega) )</td>
</tr>
<tr>
<td>2112</td>
<td>( 4kk_1^2 k_3 )</td>
<td>( \delta(\omega_1 - \Omega)\delta(\omega_2)\delta(\omega_3 - \Omega) )</td>
</tr>
<tr>
<td>2132</td>
<td>( 6kk_2 k_3 k_4 )</td>
<td>( \delta(\omega_1 + \Omega)\delta(\omega_2)\delta(\omega_3 - \Omega) )</td>
</tr>
<tr>
<td>2312</td>
<td>( 6kk_2 k_3 k_4 )</td>
<td>( \delta(\omega_1 - \Omega)\delta(\omega_2)\delta(\omega_3 + \Omega) )</td>
</tr>
<tr>
<td>2332</td>
<td>( 9kk_3^2 k_4 )</td>
<td>( \delta(\omega_1 + \Omega)\delta(\omega_2)\delta(\omega_3 + \Omega) )</td>
</tr>
<tr>
<td>2334</td>
<td>( 12kk_4 k_5 )</td>
<td>( \delta(\omega_1 + \Omega)\delta(\omega_2 + 2\Omega)\delta(\omega_3 + \Omega) )</td>
</tr>
</tbody>
</table>

Table 10.2: This table describes the thirteen terms that make up TCF A in the anharmonic approximation. The first column indicates the indices of A, B, C, and D corresponding to each term, the second column the perturbation constants \( (K) \), and the third column the delta functions \( (\delta) \) for TCF A.
Table 10.3: This table describes the thirteen terms that make up TCF B in the anharmonic approximation. The first column indicates the indices of A, B, C, and D corresponding to each term, the second column the perturbation constants (K), and the third column the delta functions (δ) for TCF B.

<table>
<thead>
<tr>
<th>Indices (ADBC)</th>
<th>K</th>
<th>δ (TCF B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0110</td>
<td>$k^2_1 k^2_2$</td>
<td>$\delta (\omega_1 + \Omega) \delta (\omega_2) \delta (\omega_3 - \Omega)$</td>
</tr>
<tr>
<td>0121</td>
<td>$2k_1 k^2_3 k_3$</td>
<td>$\delta (\omega_1 + 1) \delta (\omega_2 + 2\Omega) \delta (\omega_3 + \Omega)$</td>
</tr>
<tr>
<td>1001</td>
<td>$k^2_0 k^2_1 k_2$</td>
<td>$\delta (\omega_1 - \Omega) \delta (\omega_2) \delta (\omega_3 + \Omega)$</td>
</tr>
<tr>
<td>1021</td>
<td>$2k_0 k_1 k_2 k_3$</td>
<td>$\delta (\omega_1 + \Omega) \delta (\omega_2) \delta (\omega_3 + \Omega)$</td>
</tr>
<tr>
<td>1201</td>
<td>$2k_0 k_1 k_2 k_3$</td>
<td>$\delta (\omega_1 - \Omega) \delta (\omega_2) \delta (\omega_3 - \Omega)$</td>
</tr>
<tr>
<td>1212</td>
<td>$4k_0 k_2 k^2_3$</td>
<td>$\delta (\omega_1 + \Omega) \delta (\omega_2) \delta (\omega_3 - \Omega)$</td>
</tr>
<tr>
<td>1232</td>
<td>$6k_0 k^2_3 k_4$</td>
<td>$\delta (\omega_1 + \Omega) \delta (\omega_2 + 2\Omega) \delta (\omega_3 + \Omega)$</td>
</tr>
<tr>
<td>2110</td>
<td>$2kk_1 k^2_2$</td>
<td>$\delta (\omega_1 - \Omega) \delta (\omega_2 - 2\Omega) \delta (\omega_3 - \Omega)$</td>
</tr>
<tr>
<td>2112</td>
<td>$4kk^2_3 k_3$</td>
<td>$\delta (\omega_1 - \Omega) \delta (\omega_2) \delta (\omega_3 + \Omega)$</td>
</tr>
<tr>
<td>2132</td>
<td>$6kk_2 k_3 k_4$</td>
<td>$\delta (\omega_1 + \Omega) \delta (\omega_2) \delta (\omega_3 + \Omega)$</td>
</tr>
<tr>
<td>2312</td>
<td>$6kk_2 k^2_3 k_4$</td>
<td>$\delta (\omega_1 - \Omega) \delta (\omega_2) \delta (\omega_3 - \Omega)$</td>
</tr>
<tr>
<td>2332</td>
<td>$9kk^3 k^2_4$</td>
<td>$\delta (\omega_1 + \Omega) \delta (\omega_2) \delta (\omega_3 - \Omega)$</td>
</tr>
<tr>
<td>2334</td>
<td>$12kk_4 k_2 k_5$</td>
<td>$\delta (\omega_1 + \Omega) \delta (\omega_2 + 2\Omega) \delta (\omega_3 + \Omega)$</td>
</tr>
</tbody>
</table>
Table 10.4: Analysis of the anharmonic terms of TCFs A and B in terms of harmonic transitions. Columns one through four indicate the patterns that indices A, D, B, and C in terms of a general index i. Column five indicates the prefactors appearing in front of the perturbation constants. Columns six and seven indicates the values that frequencies \( \omega_1, \omega_2, \text{ and } \omega_3 \) take on, as enforced by each term’s delta functions. This information will be used to work towards a general relationship between anharmonic TCFs A and B.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>Value</th>
<th>( \omega_1, \omega_2, \omega_3 ) (TCF A)</th>
<th>( \omega_1, \omega_2, \omega_3 ) (TCF B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>i+1</td>
<td>i-1</td>
<td>i</td>
<td>i(i+1)</td>
<td>( \Omega, 0, -\Omega )</td>
<td>( \Omega, 0, \Omega )</td>
</tr>
<tr>
<td>i</td>
<td>i+1</td>
<td>i+1</td>
<td>i</td>
<td>(i+1)^2</td>
<td>( -\Omega, 0, -\Omega )</td>
<td>( -\Omega, 0, \Omega )</td>
</tr>
<tr>
<td>i</td>
<td>i+1</td>
<td>i+1</td>
<td>i+2</td>
<td>(i+1)(i+2)</td>
<td>( -\Omega, -2\Omega, -\Omega )</td>
<td>( -\Omega, -2\Omega, -\Omega )</td>
</tr>
<tr>
<td>i</td>
<td>i-1</td>
<td>i-1</td>
<td>i-2</td>
<td>i(i-1)</td>
<td>( \Omega, 2\Omega, \Omega )</td>
<td>( \Omega, 2\Omega, \Omega )</td>
</tr>
<tr>
<td>i</td>
<td>i-1</td>
<td>i-1</td>
<td>i</td>
<td>i^2</td>
<td>( \Omega, 0, \Omega )</td>
<td>( \Omega, 0, -\Omega )</td>
</tr>
<tr>
<td>i</td>
<td>i-1</td>
<td>i+1</td>
<td>i</td>
<td>i(i+1)</td>
<td>( -\Omega, 0, \Omega )</td>
<td>( -\Omega, 0, -\Omega )</td>
</tr>
</tbody>
</table>
Table 10.5: Based on the anharmonic oscillator approximation, ratios between TCFs A and B are presented for each possible set of delta functions giving frequencies ω₁, ω₂, ω₃ their values. The first three columns give the values of the frequencies and the fourth gives the A/B ratios.

<table>
<thead>
<tr>
<th>ω₁</th>
<th>ω₂</th>
<th>ω₃</th>
<th>A/B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ω</td>
<td>2Ω</td>
<td>Ω</td>
<td>1</td>
</tr>
<tr>
<td>−Ω</td>
<td>−2Ω</td>
<td>Ω</td>
<td>1</td>
</tr>
<tr>
<td>Ω</td>
<td>0</td>
<td>0</td>
<td>( \frac{i^2}{i(i+1)} = \frac{[i+\theta(-\omega_1)]^2}{i(i+1)} )</td>
</tr>
<tr>
<td>−Ω</td>
<td>0</td>
<td>−Ω</td>
<td>( \frac{(i+1)^2}{i(i+1)} = \frac{[i+\theta(-\omega_1)]^2}{i(i+1)} )</td>
</tr>
<tr>
<td>−Ω</td>
<td>0</td>
<td>Ω</td>
<td>( \frac{i(i+1)}{(i+1)^2} = \frac{i(i+1)}{[i+\theta(-\omega_1)]^2} )</td>
</tr>
<tr>
<td>Ω</td>
<td>0</td>
<td>−Ω</td>
<td>( \frac{i^2}{(i+1)^2} = \frac{[i+\theta(-\omega_1)]^2}{[i+\theta(-\omega_1)]^2} )</td>
</tr>
</tbody>
</table>

In Equation 10.9, \( \alpha \) denotes the maximum value that state \( i \) can attain. Since this expression is exact for a harmonic system, \( \alpha \) may be arbitrarily large. Making the sum infinite and evaluating the resulting geometric series yields the same analytical A/B ratio.
derived in Chapter 9. The anharmonic perturbation constants can easily be incorporated into Equation 10.9 to derive an anharmonic expression.

\[
\left( \frac{\sum_{i=0}^{\alpha}[i + \theta(-\omega_1)]^2 \kappa_i k_{b+1} k_{c+1} k_{d+1} e^{-i\beta \hbar \sqrt{\omega_1^2 + \omega_3^2}/2}}{\sum_{i=0}^{\alpha} i(i+1) \kappa'_i k'_{b+1} k'_{c+1} k'_{d+1} e^{-i\beta \hbar \sqrt{\omega_1^2 + \omega_3^2}/2}} \right)^{\omega_3/\omega_1 - \omega_2/2\omega_1}
\]

Equation 10.10

In Equation 10.10, the \( k \) constants are described by Table 10.1 and the \( \kappa \) constants are defined below in Equation 10.11. The primes on the denominator’s \( k \) and \( \kappa \) constants denote their association with TCF \( B \), while the ones in the denominator are associated with TCF \( A \). The \( b, c, \) and \( d \) indices corresponding to a specific \( i \) value of index \( a \) in Equation 10.10 determine the values of the \( k \) and \( \kappa \) constants.

\[
\kappa_{i=\alpha} = 1 \quad (\alpha < 1)
\]

\[
\kappa_{i=\alpha} = c_{(\alpha-1)}+ \quad (\alpha \geq 1)
\]

\[
\kappa_{i<\alpha} = 1 + c_{(i+1)-} + c_{(i-1)+}
\]

As an example, if the upper limit on the anharmonic sums is \( \alpha = 3 \), then the \( \kappa \) constants are \( \kappa_0 = k_1, \kappa_1 = k_2, \kappa_2 = 1 + c_{1+} \), and \( \kappa_3 = c_{2+} \).

Superficially, Equations 10.9 and 10.10 produce correct results, but further analysis of these expressions reveal their fatal flaws. Both of them are ill-behaved at zero frequency, a region which plays a vital role in experiments and cannot be overlooked. Additionally, in the anharmonic expression, the perturbation constants are defined by the values of \( b, c, \) and \( d \), which in turn depend on the value of index \( i \). They do not maintain
a constant value for all possible sets of delta functions. While this dependence does not formally pose any problem, it does not allow the expression to be incorporated into the TCF calculation code. Therefore, an alternative expression to relate TCFs $A$ and $B$, which remedies these issues, is considered.

\[
A_{ANH}(\omega_1, \omega_2, \omega_3) = \sum_{i=0}^{\alpha} [i + \theta(-\omega_1)] [i + \theta(-\omega_3) - \theta(\omega_2) + \theta(-\omega_2)] e^{-\beta \hbar \Omega_i} \times T_a
\]

\[
B_{ANH}(\omega_1, \omega_2, \omega_3) = \sum_{i=0}^{\alpha} [i + \theta(-\omega_1)] [i + \theta(\omega_3) - 2\theta(\omega_2) + 2\theta(-\omega_2)] e^{-\beta \hbar \Omega_i} \times T_b
\]

\[
\Omega = \sqrt{\left(\omega_1^2 + \omega_2^2\right)/2}
\]

\[
T_a = \theta(-\omega_1 \omega_3) k_i k_{i+1} k_{i+2} + \theta(\omega_1) \theta(-\omega_3) k_i^2 k_{i+1} + \theta(-\omega_1) \theta(\omega_3) k_{i+2} k_i k_{i+1} + \tanh(\beta \hbar \omega) k_i^2 k_{i+1} + 1 - \tanh(\beta \hbar \omega)
\]

\[
T_b = \theta(\omega_1 \omega_3) k_i k_{i+1} k_{i+2} + \theta(\omega_1) \theta(\omega_3) k_i^2 k_{i+1} + \theta(-\omega_1) \theta(-\omega_3) k_{i+2} k_i k_{i+1} + \tanh(\beta \hbar \omega) k_i^2 k_{i+1} + 1 - \tanh(\beta \hbar \omega)
\]

For ease of calculation, it is desirable to remove all special functions from the expression relating TCFs $A$ and $B$. In the high frequency limit, the region of interest in most typical experiments and theoretical calculations, \(\tanh(\beta \hbar \omega) = \theta(\omega) - \theta(-\omega)\). Thus, the Heavyside step functions can be written in terms of tanh functions according to the following relationships.
\[\theta(\omega) = \frac{\tanh^2(\beta\hbar\omega) + \tanh(\beta\hbar\omega)}{2}\]

\[\theta(-\omega) = \frac{\tanh^2(\beta\hbar\omega) - \tanh(\beta\hbar\omega)}{2}\] (10.13)

Using these definitions to remove the Heavyside step functions from Equation 10.12, the expression relating TCFs A and B under the anharmonic approximation is then finalized, and is displayed in Equation 10.14 below. As before, \(\Omega\) takes on a value of \(\sqrt{\omega_1^2 + \omega_3^2}/2\).

\[A_{ANH}(\omega_1, \omega_2, \omega_3) = \sum_{i=0}^{K} e^{-\beta\hbar\Omega_i} k_i T_a \times \left[ i + \frac{\tanh^2(\beta\hbar\omega_1) - \tanh(\beta\hbar\omega_1)}{2} \right] \times \left[ i + \frac{\tanh^2(\beta\hbar\omega_3) - \tanh(\beta\hbar\omega_3)}{2} - \tanh(\beta\hbar\omega_2) \right] \]

\[B_{ANH}(\omega_1, \omega_2, \omega_3) = \sum_{i=0}^{K} e^{-\beta\hbar\Omega_i} k_i T_b \times \left[ i + \frac{\tanh^2(\beta\hbar\omega_1) - \tanh(\beta\hbar\omega_1)}{2} \right] \times \left[ i + \frac{\tanh^2(\beta\hbar\omega_3) - \tanh(\beta\hbar\omega_3)}{2} - 2 \tanh(\beta\hbar\omega_2) \right] \]

\[T_a = \tanh^2[\beta\hbar(\omega_1 - \omega_3)]k_i k_{i+1} k_{i+2} + \]

\[\frac{1}{4} [\tanh^2(\beta\hbar\omega_1) + \tanh(\beta\hbar\omega_1)] [\tanh^2(\beta\hbar\omega_3) + \tanh(\beta\hbar\omega_3)] k_i^2 k_{i+1} k_{i+2} + \]

\[\frac{1}{4} [\tanh^2(\beta\hbar\omega_1) - \tanh(\beta\hbar\omega_1)] [\tanh^2(\beta\hbar\omega_3) - \tanh(\beta\hbar\omega_3)] k_{i+2}^2 k_{i+1} k_{i+2} - \]

\[\tanh^2(\beta\hbar\omega_2) k_i^2 k_{i+1} k_{i+2} + 1 - \tanh^2(\beta\hbar\omega_1) \]
\[ T_b = \tanh^2[\beta \hbar (\omega_1 + \omega_3)]k_i k_{i+1}k_{i+2} + \]
\[ \frac{1}{4} [\tanh^2(\beta \hbar \omega_1) + \tanh(\beta \hbar \omega_1)][\tanh^2(\beta \hbar \omega_3) - \tanh(\beta \hbar \omega_3)]k_i^2 k_{i+1} \kappa_i + \]
\[ \frac{1}{4} [\tanh^2(\beta \hbar \omega_1) - \tanh(\beta \hbar \omega_1)][\tanh^2(\beta \hbar \omega_3) - \tanh(\beta \hbar \omega_3)]k_{i+2}^2 k_{i+1} \kappa_i - \]
\[ \tanh^2(\beta \hbar \omega_2)k_i k_{i+1}k_{i+2} \kappa_i + 1 - \tanh^2(\beta \hbar \omega_1) \quad (10.14) \]

10.4 Relating the Real and Imaginary Parts of Anharmonic TCF \( B \)

Since only the real part of the time-domain TCF \( B \) can be calculated using classical dynamics, it is necessary to devise a relationship between TCF \( B \)'s real and imaginary parts. This is accomplished by writing out all the terms of TCF \( B \) in the time domain, separating them into their real and imaginary parts, and Fourier transforming the real and imaginary parts separately. The Fourier transforms are grouped by like delta functions into terms \( B_{jR}(\omega_1, \omega_2, \omega_3) \) and \( B_{jI}(\omega_1, \omega_2, \omega_3) \). \( R \) denotes the Fourier transform of a real part and \( I \) denotes the Fourier transform of an imaginary part. Frequency-domain relationships between individual \( B_{jR} \) and \( B_{jI} \) terms are developed and then generalized to be correct for all terms.

There are three possible groupings of delta functions associated with \( B_R \) and \( B_I \).

\[ B_{1R} : \delta(\omega_1 + \Omega) \delta(\omega_3 - \Omega) + \delta(\omega_1 - \Omega) \delta(\omega_3 + \Omega) \]
\[ B_{1I} : \delta(\omega_1 + \Omega) \delta(\omega_3 - \Omega) - \delta(\omega_1 - \Omega) \delta(\omega_3 + \Omega) \]
\[ B_{2R} : \delta(\omega_1 - \Omega) \delta(\omega_3 - \Omega) + \delta(\omega_1 + \Omega) \delta(\omega_3 + \Omega) \]
\[ B_{2I} : \delta(\omega_1 - \Omega)\delta(\omega_3 - \Omega) - \delta(\omega_1 + \Omega)\delta(\omega_3 + \Omega) \]

\[ B_{3R} : \delta(\omega_1 + \Omega)\delta(\omega_2 + 2\Omega)\delta(\omega_3 + \Omega) + \delta(\omega_1 - \Omega)\delta(\omega_2 - 2\Omega)\delta(\omega_3 - \Omega) \]

\[ B_{3I} : \delta(\omega_1 + \Omega)\delta(\omega_2 + 2\Omega)\delta(\omega_3 + \Omega) - \delta(\omega_1 - \Omega)\delta(\omega_2 - 2\Omega)\delta(\omega_3 - \Omega) \tag{10.15} \]

The constants associated with each of the \( B_{jR} \) and \( B_{jI} \) are listed below. These are the quantities used to devise relationships between the real and imaginary parts of TCF \( B \)'s terms.

\[ B_{1R} : \frac{1}{2} k_1^2 k_2^2 + 2k_0 k_2 k_3^2 e^{-\beta\hbar\Omega} + \frac{1}{2} k_0 k_1^2 k_2 e^{-\beta\hbar\Omega} + 2kk_2 k_3^2 e^{-2\beta\hbar\Omega} + \frac{9}{2} kk_3 k_4^2 e^{-2\beta\hbar\Omega} \]

\[ B_{1I} : \frac{1}{2} k_1^2 k_2^2 + 2k_0 k_2 k_3^2 e^{-\beta\hbar\Omega} - \frac{1}{2} k_0 k_1^2 k_2 e^{-\beta\hbar\Omega} - 2kk_2 k_3^2 e^{-2\beta\hbar\Omega} + \frac{9}{2} kk_3 k_4^2 e^{-2\beta\hbar\Omega} \]

\[ B_{2R} : [6kk_2 k_3 k_4 e^{-2\beta\hbar\Omega} + 2k_0 k_2 k_3^2 e^{-\beta\hbar\Omega}] \]

\[ B_{2I} : 0 \]

\[ B_{3R} : k_1 k_2 k_3 + 3k_0 k_2 k_4^2 e^{-\beta\hbar\Omega} + 6kk_4 k_5 e^{-2\beta\hbar\Omega} + kk_1 k_2^2 e^{-2\beta\hbar\Omega} \]

\[ B_{3I} : k_1 k_2 k_3 + 3k_0 k_2 k_4^2 e^{-\beta\hbar\Omega} + 6kk_4 k_5 e^{-2\beta\hbar\Omega} - kk_1 k_2^2 e^{-2\beta\hbar\Omega} \tag{10.16} \]

Table 10.6 summarizes the relationships between the real and imaginary parts of TCF \( B \) for the three different groupings of delta functions. Because the system is assumed to be in the high frequency limits, the tanh functions, which appear in the harmonic expression (Equation 9.17) and go to \( \pm 1 \) in this limit, are introduced into the relationships.

The anharmonic constants \( a, b, c, \) and \( d \) appearing in the relationships do possess \( \Omega \)-dependence, but this is not a concern since the delta functions governing the values...
Table 10.6: Based on the anharmonic oscillator approximation, ratios between the Fourier transforms of TCF $B$’s real and imaginary parts are derived. The upper portion summarizes the relationships for the three groupings of delta functions and the lower portion defines several constants used in the relationships. The $\Omega$-dependence of the constants is not a concern since the delta functions governing the values of the frequencies are the same for both the real and imaginary parts of TCF $B$. 

<table>
<thead>
<tr>
<th>Term</th>
<th>$f$, where $B_I = f \ast B_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$- \left( \frac{a-b}{a+b} \right) \tanh[\beta \hbar(\omega_1 - \omega_3 + 2\omega_2)/4]$</td>
</tr>
<tr>
<td>2</td>
<td>$- \tanh[\beta \hbar(\omega_1 - \omega_3 + 2\omega_2)/4]$</td>
</tr>
<tr>
<td>3</td>
<td>$- \left( \frac{c-d}{c+d} \right) \tanh[\beta \hbar(\omega_1 - \omega_3 + 2\omega_2)/4]$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Constant</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>$\frac{1}{2}k_1^2k_2^2 + 2k_0k_2k_3^2e^{-\beta\hbar\Omega} + \frac{9}{7}kk_3k_4^2e^{-2\beta\hbar\Omega}$</td>
</tr>
<tr>
<td>b</td>
<td>$\frac{1}{2}k_0k_1^2k_2^2e^{-\beta\hbar\Omega} + 2k_0k_2k_3^2e^{-2\beta\hbar\Omega}$</td>
</tr>
<tr>
<td>c</td>
<td>$k_1k_2^2k_3 + 3k_0k_3^2k_4e^{-\beta\hbar\Omega} + 6kk_3^2k_5^2e^{-2\beta\hbar\Omega}$</td>
</tr>
<tr>
<td>d</td>
<td>$2kk_2k_3^2e^{-2\beta\hbar\Omega}$</td>
</tr>
</tbody>
</table>
of the frequencies $\omega_1$, $\omega_2$, and $\omega_3$ are the same for both the real and imaginary parts of TCF $B$. Taking the harmonic limit of the four constants and removing the restriction of remaining in the high frequency limit, thus allowing the sums over states to become infinite, reproduces the harmonic relationship laid out in Equation 9.17.

10.5 The Final $R^{(3)}$ Expression

Having derived expressions to relate TCFs $A$ and $B$, as well as the real and imaginary parts of TCF $B$, it is now possible to derive a final expression for the third-order response function. Beginning with Equation 8.24, an exact analytical expression for $R^{(3)}$ in terms of the real and imaginary parts of TCFs $A$ and $B$, the anharmonic third-order response function is constructed.

$$R^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{i}{\hbar^3} \tanh(\beta \hbar \omega_1/2) \times$$

$$\{(1 + e^{\beta \hbar \omega_1})[1 - f_{AN}^+(\omega_1, \omega_2, \omega_3)(1 - \tanh[\beta \hbar(\omega_1 + 2\omega_2 - \omega_3)/4])] +$$

$$\quad (1 + e^{-\beta \hbar \omega_1})[1 - f_{AN}^-(\omega_1, \omega_2, \omega_3)(1 + \tanh[\beta \hbar(\omega_1 + 2\omega_2 - \omega_3)/4])]) \times$$

$$B_R(\omega_1, \omega_2, \omega_3) \quad (10.17)$$

This expression, which is expected to yield nonzero signal for the reference system collected, may be used to calculate the third-order response function using classical molecular dynamics techniques, since it is simply composed of the frequency-domain TCF $B_R(\omega_1, \omega_2, \omega_3)$ multiplied by a set of frequency factors.
Chapter 11

TCF Theory: 2D-IR Spectroscopy (Computation and Results)

In Chapters 8, 9, and 10, a time correlation function theory of two-dimensional infrared spectroscopy was developed. Specifically, these three chapters outlined the development of a theory which allowed the third-order response function $R^{(3)}$ associated with 2D-IR experiments to be calculated from a classical TCF, approximated as $B_R(t_1, t_2, t_3)$.

In this chapter, the practical aspects of obtaining $R^{(3)}(\omega_1, \omega_2, \omega_3)$ from $B_R(t_1, t_2, t_3)$, including accounting for a constant time delay $t_2$, Fourier transforming the time-domain TCF, and incorporating a reliable quantum correction scheme, will be discussed. Additionally, the issue of using $R^{(3)}$ to compute third polarization $P^{(3)}$, the observable in a 2D-IR experiment, is explored.

Finally, the application of the TCF theory to neat water$^{88,98}$ and 1,3-cyclohexanedione in deuterated chloroform$^{99}$, two systems which have been probed experimentally, will be presented. The resulting spectra for both systems are in agreement with experimental results and demonstrate the promise of this TCF theory to accurately reproduce 2D-IR spectra of condensed phase systems.
11.1 The Steps in Calculating a 2D-IR Spectrum

The computation of a two-dimensional infrared spectrum from classical molecular dynamics is accomplished in several steps.

First, to obtain a series of time-ordered position configurations for the system of interest, microcanonical (NVE) classical molecular dynamics simulations are performed using a code developed at the Center for Molecular Modeling at the University of Pennsylvania.\textsuperscript{15,16} The code employs reversible integration and extended system techniques. Position configurations are stored frequently enough to resolve the relevant frequencies. For example, in computing the spectrum of neat water, configurations were stored every 4.0 fs, giving a Nyquist frequency of 4167 cm\(^{-1}\).\textsuperscript{98,100}

Once the configurations are obtained, it is necessary to calculate the dipole \(\mu\) at every step of the simulation and use the results to obtain the four-point dipole correlation function \(\langle \mu_j(t_1 + t_2)\mu_i(t_1 + t_2 + t_3)\mu_k(t_1)\mu_\ell(0) \rangle\). In these calculations, a point atom polarizability approximation (PAPA) model,\textsuperscript{101} which accounts for the interaction of dipoles with the field created by other dipoles in the system, is employed.

The induced dipole associated with atom \(i\) consists of contributions from the external electric field and all the other induced dipoles \(j\) in the system. In a system of \(N\) atoms, atom \(i\)'s induced dipole is given below.

\[
\mu_i = \alpha_i \left[ E_i - \sum_{j=1,i\neq j}^N T_{ij} \mu_j \right] \tag{11.1}
\]
In Equation 11.1, $E_i$ is the applied electrical field at point $i$, $\alpha_i$ is the polarizability tensor of $i$, and $T_{ij}$ is the dipole field tensor. The dipole field tensor is traceless and describes the interaction of atoms $i$ and $j$, as shown below.

$$T_{ij} = -\frac{3}{r^5} \begin{pmatrix} x^2 - 1/3r^2 & xy & xz \\ xy & y^2 - 1/3r^2 & yz \\ xz & yz & x^2 - 1/3r^2 \end{pmatrix}$$  \quad (11.2)$$

In Equation 11.2, $r$ represents the distance between atoms $i$ and $j$ and $x$, $y$, and $z$ are the Cartesian components of the vector from point $i$ to point $j$. At this point, Equation 11.1 is rewritten to solve for the many body polarizability.

$$\alpha_i^{-1} \mu_i + \sum_{j=1, i \neq j}^{N} T_{ij} \mu_j = E_i$$  \quad (11.3)$$

Equation 11.3 can be recast as a matrix equation.

$$\begin{pmatrix} \alpha_1^{-1} & T_{12} & \ldots & T_{1N} \\ T_{21} & \alpha_2^{-1} & \ldots & T_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ T_{21} & \ldots & \ldots & \alpha_N^{-1} \end{pmatrix} \begin{pmatrix} \mu_1 \\ \mu_2 \\ \vdots \\ \mu_N \end{pmatrix} = \begin{pmatrix} E_1 \\ E_2 \\ \vdots \\ E_N \end{pmatrix}$$  \quad (11.4)$$

A $3N \times 3N$ matrix $A$ is defined such that Equation 11.4 becomes $A \mu = E$. Solving for $\mu$ yields the equation $\mu = BE$, where $B$ is simply the inverse of matrix $A$. $B$ is made up of $N$ 3 x 3 matrices $B_{ij}$. 

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The matrix Equation 11.4 can now be written as a set of \( N \) equations for the individual atoms’ induced dipoles.

\[
\mu_i = \left[ \sum_{j=1}^{N} B_{ij} \right] E \tag{11.6}
\]

Equation 11.6 assumes that the electrical field \( E \) is uniform for all points \( i \). Finally, this equation can be used to determine the system’s total induced dipole.

\[
\mu_{\text{system}} = \sum_{i=1}^{N} \mu_i = \left[ \sum_{i=1}^{N} \sum_{j=1}^{N} B_{ij} \right] E \tag{11.7}
\]

The PAPA model has been successfully used to quantitatively reproduce the linear infrared spectrum of water \(^{19,102}\) and the SFG spectrum of the water/vapor interface \(^{103}\) and therefore appears to be a suitable model for these calculations.

Once the TCF \( \langle \mu_j(t_1+t_2)\mu_i(t_1+t_2+t_3)\mu_k(t_1)\mu_\ell(0) \rangle \) has been obtained, it is Fourier transformed to obtain \( B_R(\omega_1, \omega_2, \omega_3) \). The result is multiplied by a set of frequency factors as described in Equation 9.20 for the harmonic reference system or Equation 10.17 for the anharmonic system to obtain \( R^{(3)}(\omega_1, \omega_2, \omega_3) \). The response function is then reverse
Fourier transformed to the time domain and can then be applied to Equation 8.1 to obtain the third order polarization \( P^{(3)}(t) \). Finally, a Fourier Laplace transform of the polarization gives the 2D-IR spectrum in the frequency domain.

### 11.2 Considering a Constant \( t_2 \) Delay

The theory presented in the previous chapters is a fully three-dimensional theory. Expressing the third-order response function as a single classical TCF multiplied by frequency factors is a tremendous simplification, but the computation of a three-time correlation is a demanding task.

At this point, it is worth considering the possibility of implementing a two-dimensional theory, since many 2D-IR experiments fix the time delay \( t_2 \) at set values, often zero. In assessing the validity of such a theory, it is important to consider if these experiments do, indeed, probe a two-dimensional response function and if such a response function is determined by a two-dimensional classical correlation function.

In the 2D-IR echo experiment, the time delay \( t_2 \) is set to zero. For finite pulse lengths, this equality is not literally enforced, but as an approximation to realistic experimental conditions, the value of \( t_2 \) is restricted using a delta function. Under such conditions, the Fourier transform of the time-domain response function \( R^{(3)}(t_1, t_2 = 0, t_3) \) is given by

\[
R^{(3)}(\omega_1, \omega_3) = R^{(3)}(\omega_1, t_2 = 0, \omega_3) \\
\left(\frac{1}{2\pi}\right)^3 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-i\omega_1 t_1} e^{-i\omega_2 t_2} e^{-i\omega_3 t_3} R^{(3)}(t_1, t_2, t_3) \delta(t_2) dt_1 dt_2 dt_3
\]  

(11.8)
Equation 11.8 suggests that a means of calculating $R^{(3)}(t_1, t_3)$ with $t_2 = 0$ is required to obtain a two-dimensional response function. However, determining the reverse Fourier transform of Equation 9.20 or 10.17, $B_R$ multiplied by a complicated set of frequency factors, then calculating its value for $t_2 = 0$ is an extremely difficult task.

Using the proposed methods, the most convenient way of imposing the restriction on $t_2$ is to calculate the two-dimensional correlation function $B_R(t_1, t_2 = 0, t_3)$. The TCF is then Fourier transformed to obtain $B_R(\omega_1, t_2 = 0, \omega_3)$ and multiplied by a set of frequency factors to obtain $R^{(3)}(\omega_1, \omega_2, \omega_3)$. Reverse Fourier transforming gives the final result, $R^{(3)}(t_1, t_2 = 0, t_3)$.

\[
R^{(3)}(t_1, t_2 = 0, t_3) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{i\omega_1 t_1} e^{i\omega_2 t_2} e^{i\omega_3 t_3} \times h(\omega_1, \omega_2, \omega_3) B_R(\omega_1, \omega_2, \omega_3) d\omega_1 d\omega_2 d\omega_3 \bigg|_{t_2 = 0} \tag{11.9}
\]

One complication with this procedure is that, if $h(\omega_1, \omega_2, \omega_3)$ has any $\omega_2$ dependence, it will not necessarily follow that the final time-domain result is evaluated for $B_R(t_1, t_2 = 0, t_3)$. However, for $\beta \hbar \omega_{1,2,3} >> 1$, the frequency range of interest in many 2D-IR experiments, it can be shown that the $\omega_2$ dependence of $h(\omega_1, \omega_2, \omega_3)$ weakens significantly. When all frequencies are approximately $3000 \text{ cm}^{-1}$, the $\omega_2$ dependence is weak, and when $\omega_2$ is increased to $6000 \text{ cm}^{-1}$, it virtually disappears.\(^{98}\) The value of $h(\omega_1, \omega_2, \omega_3)$ changes minimally over the width of an intramolecular resonance and has little effect on the resulting lineshapes. Thus, in the high frequency limit, the function $h$ can be essentially be written as $h(\omega_1, \omega_3)$. Consequently, the selection of a large $\omega_2$
and evaluation of Equation 11.9 using \( B_R(\omega_1, t_2 = 0, \omega_3) \) are appropriate actions and give reliable results.

In the results displayed in this chapter, \( B_R \) is calculated and Fourier transformed as a two-dimensional correlation function with a constant value of \( t_2 \). While this approximation gives credible results, the calculation of a three-dimensional correlation function is still considered the most accurate way to obtain a 2DIR signal from classical MD trajectories. The development of codes to handle the full three-dimensional theory is underway.

11.3 Fourier Transforming \( B_R(t_1, t_2, t_3) \)

To correctly transform the TCF \( B_R(t_1, t_2, t_3) \) to the frequency domain, it is necessary to perform a full Fourier transform to account for all positive and negative values of the times.

\[
B_R(\omega_1, \omega_2, \omega_3) = \left( \frac{1}{2\pi} \right)^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-i\omega_1 t_1} e^{-i\omega_2 t_2} e^{-i\omega_3 t_3} \times \\
\langle \mu_j(t_1 + t_2) \mu_i(t_1 + t_2 + t_3) \mu_k(t_1) \mu_l(0) \rangle \delta(t_2 - \tau_2) \quad (11.10)
\]

The delta function in Equation 11.10 holds \( t_2 \) constant at delay \( \tau_2 \), as described in the previous section. To implement this Fourier transform correctly, it is necessary to calculate \( B_R(t_1, \tau_2, t_3) \) in four quadrants in order to include all positive and negative values of \( t_1 \) and \( t_3 \). Calculating all four quadrants essentially amounts to calculating four classical TCFs expressed in terms of positive and negative values of \( t_1 \) and \( t_3 \).
\[
B^{++} = \langle \mu_j(t_1 + \tau_2)\mu_i(t_1 + t_3 + \tau_2)\mu_k(t_1)\mu_\ell(0)\rangle
\]
\[
B^{+-} = \langle \mu_j(t_1 + \tau_2)\mu_i(t_1 - t_3 + \tau_2)\mu_k(t_1)\mu_\ell(0)\rangle
\]
\[
B^{-+} = \langle \mu_j(-t_1 + \tau_2)\mu_i(-t_1 + t_3 + \tau_2)\mu_k(-t_1)\mu_\ell(0)\rangle
\]
\[
B^{--} = \langle \mu_j(-t_1 + \tau_2)\mu_i(-t_1 - t_3 + \tau_2)\mu_k(-t_1)\mu_\ell(0)\rangle
\] (11.11)

Time stationarity properties of the TCFs can be used to rewrite the four quadrants’ TCFs in terms of only positive times.\textsuperscript{34,98}

\[
B^{++} = \langle \mu_j(t_1 + \tau_2)\mu_i(t_1 + t_3 + \tau_2)\mu_k(t_1)\mu_\ell(0)\rangle
\]
\[
B^{+-} = \langle \mu_j(t_1 + t_3 + \tau_2)\mu_i(t_1 + \tau_2)\mu_k(t_1 + t_3)\mu_\ell(t_3)\rangle
\]
\[
B^{-+} = \langle \mu_j(\tau_2)\mu_i(\tau_2)\mu_k(0)\mu_\ell(t_3)\rangle
\]
\[
B^{--} = \langle \mu_j(t_3 + \tau_2)\mu_i(\tau_2)\mu_k(t_3)\mu_\ell(t_1 + t_3)\rangle
\] (11.12)

For \(\tau_2 = 0\), the TCFs corresponding to the diagonal quadrants \(B^{++}\) and \(B^{--}\) are equal, and so are the ones corresponding to the off-diagonal quadrants, \(B^{+-}\) and \(B^{-+}\). This is proven using time reversal, \textit{i.e.} making all the time arguments negative, which does not change the TCF. Thus, having \(\tau_2 = 0\) requires the calculation of only two TCFs, \(B^{++}\) and \(B^{+-}\).

For nonzero \(\tau_2\), none of the four TCFs are equal, making it necessary to calculate all of them separately. Once the appropriate TCFs have been calculated, the full Fourier transform may then be performed to obtain \(B_R(\omega_1, t_2 = \tau_2, \omega_3)\).
Although calculations will generally be performed in the high frequency limit, it is interesting to note that, in the classical limit, the time-domain response function is simply written as a sum of time derivatives of $B_R(t_1, t_2, t_3)$. In this case, it is possible to examine only the positive quadrant $B^{++}$ since the Fourier transform of $B_R(t_1, t_2, t_3)$ is not required to obtain the response function.

### 11.4 Implementing a Quantum Correction Scheme

Equating the real part of $B(t_1, t_2, t_3)$ with the classical TCF $\langle \mu_j(t_1 + t_2)\mu_i(t_1 + t_2 + t_3)\mu_k(t_1)\mu_\ell(0) \rangle$ is an approximation, commonly implemented in the case of one time correlations. To make the classical TCF closer in form to its quantum mechanical counterpart, a quantum correction scheme may be applied. Such a scheme simply involves multiplying the Fourier transform of the classical TCF by a set of frequency factors, which is derived by dividing the quantum mechanical $B_R(\omega_1, \omega_2, \omega_3)$ by its classical limit.

Under the harmonic reference system, two distinct quantum correction schemes were developed for the theory of $R^{(3)}$ and tested for plausibility. The quantum correction schemes were constructed using the six lowest order terms contributing to TCF $B$, i.e. the $B^{1111}$ terms displayed in Equation 9.11.

\[
B^Q_R(\omega_1, \omega_2, \omega_3) = \frac{\beta \hbar \omega_1}{8} \left[ (\omega_1 - \omega_3 + 2\omega_2) \coth^2(\beta \hbar \omega_1/2) + (\omega_1 + \omega_3 - 2\omega_2) \csch^2(\beta \hbar \omega_1/2) \right] B^C(\omega_1, \omega_2, \omega_3) \tag{11.13}
\]
\[ B_R^Q(\omega_1, \omega_2, \omega_3) = \frac{\beta \hbar \omega_1}{8} \left[ (\omega_3 - \omega_1 + 2\omega_2) \coth(\beta \hbar \omega_3/2) + (\omega_1 + \omega_3 - 2\omega_2) \text{csch}^2(\beta \hbar \omega_3/2) \right] B_C(\omega_1, \omega_2, \omega_3) \] (11.14)

In Equations 11.13 and 11.14, \( B_R^Q \) represents the Fourier transform of the real part of the quantum time correlation function \( B \) and \( B_C \) represents its classical limit. The two proposed quantum correction schemes represent the simplest functional forms that can exactly relate \( B_R^Q \) and \( B_C \) for the harmonic reference system.

Equation 11.13 may be considered the more reasonable of the two quantum correction schemes because it predicts zero signal along the \( \omega_3 \) axis with \( \omega_1 = 0 \). This behavior is congruent with Equation 9.20, whose \( \tanh(\beta \hbar \omega_1/2) \) prefactor suggests that the response function is zero when \( \omega_1 = 0 \) in the classical limit. In contrast, the scheme described by Equation 11.14 gives no signal along the \( \omega_1 \) axis with \( \omega_3 = 0 \), behavior that is not predicted by Equation 9.20.

11.5 Calculating Polarization

Once the response function \( R(3) \) has been computed, the next step in obtaining the 2D-IR signal is to calculate the third-order polarization \( P^{(3)}(t) \) as in Equation 8.1. To obtain a more explicit expression for \( P^{(3)} \), the time envelopes of the applied electric fields \( E_{1\ell}, E_{2k}, \) and \( E_{3j} \) must be specified.

The simplest time envelope is the \( \delta \)-function, which results in \( P^{(3)} \) proportional to \( R^{(3)} \). Using \( \delta \)-function time envelopes eliminates the need to perform the integrations required in Equation 8.1, but has the unfortunate consequence of removing the dependence
of $P^{(3)}$ on the experimental wave-matching conditions.$^{58,59}$ It is also necessary to consider that in a frequency-domain experiment, it is possible to generate a nearly monochromatic pulse, but in the time-domain experiments of interest in this research, $\delta$-function time envelopes are not realistic. For theoretical studies performed in the impulsive limit, it is common to invoke the rotating wave approximation, which preserves only resonant terms, in which the optical frequency is cancelled by a material frequency of opposite sign, of the response function, and thereby takes into account phase-matching conditions. Since this theory of two-dimensional infrared spectroscopy involves the full third-order response function, it is incorrect to derive $P^{(3)}$ from $R^{(3)}$ using $\delta$-function pulses.$^{34}$ The inclusion of wave-matching conditions is required to highlight the Liouville pathways of interest for a particular experiment.

One possible approach to this problem is to select a field time envelope function consistent with those used in experiments, such as a Gaussian function, which retains the wavevector associated with each electric field. A Gaussian time envelope takes on the following form, where $\sigma$ is a parameter indicating its width.

$$E(t) = \cos[\omega(t)]e^{-t^2/\sigma} \quad (11.15)$$

Because in the experiments the time delay $\tau_2$ is typically set to a constant $\tau_0$, a $\delta$-function envelope is used for the second electric field $E_{2j}$ and another $\delta$-function is used to enforce the time’s constant value. If the dynamics of interest occur on a much longer time scale than the pulses, it is acceptable to assume that $\tau_n = t_n$.$^{63}$
\[ P^{(3)}(\tau_1, \tau_2 = \tau_0, t) = \int_0^\infty \int_0^\infty dt_1 dt_2 dt_3 R^{(3)}(t_1, t_2, t_3) E_3(t - t_3) \times \\
E_2(t + \tau_2 - t_3 - t_2) E_1(t + \tau_1 + \tau_2 - t_3 - t_2 - t_1) \delta(\tau_2 - \tau_0) \]

\[ E_1(t + \tau_1 + \tau_2 - t_3 - t_2 - t_1) = \cos[\omega_1(t + \tau_1 + \tau_2 - t_3 - t_2 - t_1)] \times \\
e^{(t+\tau_2+\tau_1-t_3-t_2-t_1)^2/\sigma} \]

\[ E_2(t + \tau_2 - t_3 - t_2) = \delta(t + \tau_2 - t_3 - t_2) \]

\[ E_3(t - t_3) = \cos[\omega_3(t - t_3)]e^{(t-t_3)^2/\sigma} \quad (11.16) \]

The \( \delta \)-functions in Equation 11.16 can be enforced and the final result can be adapted to numerical computational methods in order to obtain the third-order polarization from the calculated response function \( R^{(3)} \).

11.6 Ambient Water

The successful application of this TCF theory to ambient water demonstrates its potential to correctly capture the 2D-IR spectra of condensed phases. Since water is difficult to investigate experimentally due to the strong infrared absorbance of the OH oscillator, most experimental studies have focused on dilute solutions of HOD in liquid \( \text{D}_2\text{O} \). However, the 2DIR spectrum of neat water has recently been determined using a transient grating experiment. The 2DIR spectrum of water, particularly in the OH stretching region, can provide insight into the distribution of hydrogen bonds in the condensed phase. The presence of off-diagonal peaks in the spectrum might sug-
gest coupling of oscillators through hydrogen bonds or mechanisms such as dipole-dipole coupling, which would facilitate the transfer of vibrational energy between molecules.88

The results of calculations on neat water might serve as a benchmark for assessing the validity of the TCF theory. Beginning with a system of ambient water, the two-time correlation function of the system dipole $B_R(t_1, t_3)$ was calculated for several fixed values of time delay $\tau_2$ then used to determine the response function $R^{(3)}(\omega_1, \omega_2)$.

To generate the time-ordered position configurations required for TCF calculations, microcanonical classical molecular dynamics simulations15 were carried out on a system of 64 flexible SPC water molecules. In a previous study, it was demonstrated that a system size of 64 molecules was sufficient to reproduce the linear infrared spectrum of water,19 and was therefore considered reasonable for these calculations. The water was simulated at a density of 0.99 g/cm$^3$ and an ambient temperature of 295 K, conditions producing a pressure of 1.0 atm, as determined by isobaric-isothermal (NPT) molecular dynamics. The water intramolecular potential included a harmonic bending potential, linear cross terms, and a Morse OH stretching potential.19,103 Simulations were composed of 1.4 million 1.0 fs time steps and position configurations were stored every 4.0 fs (allowing for resolution of the Nyquist frequency), yielding a total of 350,000 configurations. The molecular dynamics was performed without explicit polarization forces, but the point atomic polarizability (PAPA) model, which explicitly includes many-body polarizability, was used to calculate the time dependent dipole of the liquid water. Additionally, a permanent dipole model, fit to ab initio calculations,106 was adopted in these simulations. Induced dipole derivatives, accounted for by the PAPA model, are respon-
sible for most of the observed liquid state infrared intensity in the OH stretching region, while the bending intensity is mostly determined by the permanent dipole derivative.

For the time delay \( \tau_2 = 0 \) the two TCFs \( B^{++} \) and \( B^{+-} \) shown in Equation 11.11 were calculated. The TCFs decayed slowly\(^{107} \) and were calculated using a maximum correlation time of 20\( \text{ps} \) in the \( t_1 \) and \( t_3 \) directions. Over the course of 20 ps, each TCF decayed to approximately 10 percent of its initial value, but did not reach the asymptotic value of zero.\(^98 \) Ideally, longer correlation times would allow the TCFs to decay fully to zero, but the computational demands became too great for such correlation times to be practical. A correlation time of 50 ps, which would have allowed the TCF to decay to one percent of its initial value, would have required the storage and manipulation of several gigabytes of data.

To effectively Fourier transform the TCF data, baseline values for individual time slices were subtracted from the data and a series of one-dimensional Fourier transforms was performed. This procedure did not affect the lineshape, as compared to the Fourier transform of a TCF that fully decayed to zero.

Figure 11.1 displays the magnitude of the Fourier transform of the fully polarized correlation function \( B_R(t_1, t_2 = 0, t_3) \). Multiplying this result by either the harmonic or anharmonic frequency factors would give the third-order response function. A strong diagonal signal, which is similar in appearance to water’s linear IR spectrum and indicates strong self-coupling of vibrational modes,\(^82 \) is present, as shown in Figure 11.2. Dominant peaks are present near 1800 \( \text{cm}^{-1} \) and 3300 \( \text{cm}^{-1} \), liquid water’s infrared bending and stretching regions, respectively. Slowly decaying ridges are present along the \( \omega_3 \) axis.
Figure 11.1: The magnitude of the Fourier transform of the two time correlation function of the system dipole $|B_R(\omega_1, t_2 = 0, \omega_3)|$ for ambient water. The intramolecular stretching region is displayed.
Figure 11.2: A one-dimensional slice of the frequency-domain TCF $B_R(\omega_1, \omega_3)$ corresponding to the diagonal, $\omega_1 = \omega_3$ is displayed. This slice is smoothed using a single multipoint average in both frequency directions to eliminate oscillations near and along the diagonal.

at $\omega_1 = 1800 \text{ cm}^{-1}$ and $3300 \text{ cm}^{-1}$. These ridges suggest coupling between water’s bending and stretching modes. Although water has distinct antisymmetric and symmetric stretches in the gas phase, the “mixing” of these resonances in the condensed phase results in the broad infrared absorption$^{17-19}$ that is clearly shown in the behavior of this correlation function.

One-dimensional frequency slices of $B_R(\omega_1, \omega_2)$ reveal the detailed line shapes associated with this TCF, as well as the nature of the off-diagonal couplings. In Figure 11.2 a diagonal slice of $B_R(\omega_1, \omega_3)$, which is reminiscent of the linear IR experiment, is displayed. The opposite phase of the bending and stretching modes should be noted, and
Figure 11.3: Theoretical spectra for ambient water are displayed. The upper panel shows the linear IR spectrum of water, and the bottom panel is a contour plot of the third-order response function calculated under the harmonic approximation.

may be used to extract structural information about the system being probed, such as the relative orientations of transition dipoles of coupled vibrational modes.\textsuperscript{62}

Figure 11.3 displays the third-order response function calculated under the harmonic approximation. The contour plot reveals a strong echo signal along the diagonal with peaks at 1850 and 3300 cm\textsuperscript{-1}. The diagonal peak at 3300 cm\textsuperscript{-1} is elongated parallel to the diagonal, indicative of inhomogeneous broadening, and also at an angle to the diagonal and parallel to the $\omega_3$ axis, suggesting lifetime broadening.\textsuperscript{60}

The magnitude of the off-diagonal signal is small compared to the diagonal, but significant signal is still visible in these regions. The broad and extensive couplings that
Figure 11.4: Two frequency slices of the harmonic third-order response function for neat water are displayed. The slices are taken along $\omega_1$ with $\omega_3 = 1850$ wavenumbers (left panel) and $\omega_3 = 3300$ wavenumbers (right panel). The insets highlight the off-diagonal couplings between water's bending and stretching modes. The features that appear in water’s third-order response function are consistent with the fast vibrational energy distribution that is frequently observed in water’s behavior.\textsuperscript{108,109}

Figure 11.4 demonstrates the prominence of off-diagonal couplings in water’s 2D-IR spectrum. The left panel presents a slice of water’s harmonic third-order response function along $\omega_1$ with $\omega_3 = 1850$ cm$^{-1}$. The water bending peak, a diagonal, is centered at $\omega_1 = 1850$ cm$^{-1}$, and the inset highlights its weaker coupling with the OH stretch at around 3300 cm$^{-1}$. The right panel displays a slice along $\omega_1$ with $\omega_3 = 3300$ cm$^{-1}$. The dominant diagonal peak at $\omega_1 = 3300$ cm$^{-1}$ represents the OH stretch, and a weak coupling with the bending mode at $\omega_1 = 1850$ cm$^{-1}$ appears in the inset.

Figure 11.5 displays the use of the quantum correction scheme described by Equation 11.13. A diagonal ($\omega_1 = \omega_3$) slice of the quantum corrected third-order response
Figure 11.5: A diagonal slice of the quantum corrected third-order response function of neat water is displayed. The inset highlights the detailed lineshape. The quantum correction affects the magnitude of the signal, but does not change the lineshape significantly.
function indicates that the quantum correction scheme only significantly affects the magnitude of the signal. The line shape remains essentially unchanged from its appearance in Figure 11.4. This result is consistent with observations of one-dimensional spectroscopies, for which quantum corrections are typically flat functions over the width of vibrational resonances\textsuperscript{17,32} and only slightly affect the lineshape of the signal. The minimal effect of applying a quantum correction scheme to the third-order response function implies that the TCF theory is capable of capturing the essential features of 2D-IR spectroscopy without quantum correction.

Water’s third-order response function was also calculated for several different population times $\tau_2$, and the results were found to be consistent with the behavior of existing experimental spectra.\textsuperscript{88} As displayed in Figure 11.6, the off-diagonal couplings become more prominent as population relaxation and dephasing take place.\textsuperscript{110} Looking specifically at the OH stretching region, the spectrum corresponding to $\tau_2 = 0$ exhibits inhomogeneous broadening in the elongation of the diagonal peak. When the waiting time is increased to 48 and 100 fs, the peak becomes less elongated, suggesting rapid relaxation and memory loss in the system. It has been suggested that this relaxation can be attributed to fast librational motions having a period between 30 and 90 fs in the hydrogen bond network of liquid water.\textsuperscript{88}

In applying the TCF theory of 2D-IR spectroscopy to neat water, a system whose properties are well established through numerous theoretical and experimental studies, the potential of the theory to correctly capture 2D-IR signal and couplings was clearly demonstrated.
Figure 11.6: The water rephasing signal in the OH stretching region for $\tau_2 = 0$ fs (top), 48 fs (middle) and 100 fs (bottom) is displayed. The elongated peak for $\tau_2 = 0$ suggests the presence of inhomogeneous broadening, which is lost by 50 fs.
Figure 11.7: *These simulation snapshots illustrate the stretching modes, indicated by yellow vectors, of 1,3-cyclohexanedione. The two modes of interest are the symmetric stretch (left panel) at 1711 wavenumbers and the antisymmetric stretch (right panel) at 1735 wavenumbers.*

11.7 1,3-Cyclohexanedione

1,3-cyclohexane has two carbonyl groups which give symmetric and antisymmetric stretching bands at 1711 and 1735 cm$^{-1}$ in the linear infrared spectrum.\textsuperscript{99} The nature of 1,3-cyclohexanedione’s bending and stretching modes is displayed in Figure 11.7.

A recent 2D-IR experiment revealed cross peaks describing the coupling of these two stretching modes. The simplicity of this molecule and the availability of experimental results makes 1,3-cyclohexanedione an ideal model system for testing the TCF theory of 2D-IR spectroscopy. Molecular dynamics calculations on 1,3-cyclohexanedione solvated by 64 CDCl$_3$ molecules were performed to generate a series of time-ordered position configurations. The configurations were stored every 8 fs in order to resolve the frequencies of interest. A model proposed by Dietz and Heinzinger\textsuperscript{111} and Applequist
Figure 11.8: A calculated linear infrared spectrum of solvated 1,3-cyclohexanedione is displayed. The inset highlights the carbonyl stretching region. The symmetric and antisymmetric stretching bands appear at 1705 and 1760 wavenumbers, respectively.

Polarizabilities\textsuperscript{112} were employed to model the solvent, and Amber 94 parameters\textsuperscript{22} to model the 1,3-cyclohexanedione. A theoretical linear infrared spectrum, displayed in Figure 11.8 of the system showed the expected symmetric and antisymmetric stretching bands around 1705 and 1760 cm\textsuperscript{−1}.

Next, the two-dimensional infrared spectrum of 1,3-cyclohexanedione, displayed in Figure 11.9, was calculated with $\tau_2 = 0$. The Fourier-Laplace transform of the system’s third-order polarization, calculated under the anharmonic approximation, exhibited a strong diagonal signal with peaks near 1690 and 1740 cm\textsuperscript{−1}, as expected from examination of the system’s linear IR spectrum, and a broad off-diagonal ridge along $\omega_1$ centered at $\omega_3 = 1670$ cm\textsuperscript{−1}. The appearance of this ridge suggests the presence of coupling between...
Figure 11.9: The Fourier-Laplace transform of the third-order polarization of 1,3-cyclohexanedione, calculated under the anharmonic approximation, is displayed. A strong diagonal signal with peaks at 1690 and 1740 wavenumbers and an off-diagonal ridge along $\omega_1$ with $\omega_3 = 1670$ wavenumbers are present.

The stretching modes and another mode with frequency of 1670 cm$^{-1}$. A frequency slice of the diagonal ($\omega_1 = \omega_3$), shown in Figure 11.10 confirms the existence of peaks at 1690 and 1740 cm$^{-1}$. As in the experimental spectrum, both peaks have a positive phase.$^{99}$

Taking frequency slices of the 2D-IR signal highlights off-diagonal couplings between the symmetric and asymmetric stretching modes. Figure 11.11 shows slices along $\omega_1$ with $\omega_3 = 1682$ and 1723 cm$^{-1}$. The plot along $\omega_1$ with $\omega_3 = 1682$ cm$^{-1}$ has a strong positive peak centered at $\omega_1 = 1682$ cm$^{-1}$ corresponding to the symmetric stretching mode’s diagonal signal, as well as a negative peak at centered at $\omega_1 = 1723$ cm$^{-1}$, which
Figure 11.10: The Fourier-Laplace transform of the third-order polarization of 1,3-cyclohexanedione is displayed for $\omega_1 = \omega_3$. The diagonal exhibits two strong positive peaks at 1690 and 1740 wavenumbers, as does the experimental spectrum.
suggests coupling with the antisymmetric stretching mode. The plot along $\omega_1$ with $\omega_3 = 1723$ cm$^{-1}$, similarly, exhibits a large positive diagonal peak at $\omega_1 = 1723$ cm$^{-1}$ corresponding to the antisymmetric stretch and a smaller negative peak at $\omega_1 = 1682$ cm$^{-1}$ to indicate coupling with the symmetric stretching mode. As in the experimental spectrum of 1,3-cyclohexanedione, there is a change in phase between the diagonal and off-diagonal peaks, which indicates that the angle between the transition dipoles of the symmetric and antisymmetric stretching modes is ninety degrees, a value larger than the magic angle of 54.7 degrees.$^{99,113,114}$

The calculated spectrum of 1,3-cyclohexanedione is in strong agreement with the experimental spectrum and, just like the neat water system, supports the reliability of the time correlation function theory of two-dimensional infrared spectroscopy.
Figure 11.11: Two frequency slices of 1,3-cyclohexanedione’s third-order polarization are displayed. The slices are taken along $\omega_1$ with $\omega_3 = 1682$ (top panel) and 1723 (bottom panel) wavenumbers. The slices highlight the off-diagonal couplings between the symmetric and antisymmetric stretching modes.
Chapter 12

Conclusions

In this dissertation, the strong potential of computationally tractable molecular dynamics and time correlation function techniques to provide microscopic understanding of experimental results has been clearly demonstrated via the results of two separate investigations, the calculation of molecular volumes using molecular dynamics techniques and the derivation of a time correlation function theory of two-dimensional infrared spectroscopy.

Isobaric-isothermal (NPT) molecular dynamics simulations can effectively be used to calculate time-dependent molecular volumes in conjunction with photothermal experiments, such as photoacoustic calorimetry (PAC), as demonstrated in the case of the trans – cis isomerization of azobenzene and the solvation of anionic methane. The determination of a statistically significant volume change using these computational methods can potentially identify the presence of short-lived metastable intermediates associated with chemical processes such as peptide folding. Computational tools including simulation snapshots and radial distribution functions impart detailed microscopic knowledge of the structural changes and dynamics accompanying molecular volume changes.

The theoretical investigations outlined in Chapters 3 and 4 corroborate experimental
results and additionally provide an atomistic level of understanding of the forces and structural factors that drive molecular volume changes. This synergistic approach to determining and interpreting molecular volume changes may easily be applied to complex biomolecules and other interesting systems.

The development of a time correlation function theory of two-dimensional infrared (2D-IR) spectroscopy serves to decrease a complicated quantum mechanical problem to the calculation of a single classical time correlation function, a quantity that can be computed using molecular dynamics techniques. While an exact expression for the third-order response function, which determines 2D-IR signal, could not be derived, the invocation of harmonic and anharmonic approximations yielded credible theoretical 2D-IR spectra of neat water and 1,3-cyclohexanedione in deuterated chloroform. Preliminary computational results hint at the promise of this time correlation function theory to reveal anharmonic couplings and time-dependent three-dimensional structures of organic molecules and peptides, as the experiments do. Accurate processing of calculated time correlation functions and the application of the theory in three dimensions are continuing areas of research which are expected to dramatically improve the reliability and clarity of calculated spectra. Once a solid theoretical foundation for determining 2D-IR spectra is established, it will be a helpful tool for reproducing and examining the results of current 2D-IR experiments on a microscopic level. The ability of molecular dynamics coupled with this time correlation function theory of 2D-IR spectroscopy to model intricate condensed phase systems may ultimately help the scientific community overcome the challenge of interpreting the dynamics that determine 2D-IR spectra.
The endeavors of calculating molecular volume and determining 2D-IR spectra outlined in this work indicate the strong synergy between experimental and theoretical work. When solid theoretical methods are developed and carefully refined using simple model systems, they may serve to predict the behavior of interesting chemical systems in different environments. Using theory and experiment together, as with these two research projects, is a powerful method of providing detailed, atomistic interpretations of a variety of chemical phenomena.
References


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About the Author

Christina R. Kasprzyk received a Bachelor’s of Arts Degree from the University of South Florida in May of 2000. In Fall 2001, she entered the Doctoral program at the University of South Florida and immediately began work in computational and theoretical chemistry with Professor Brian Space.

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