Solvation Structures and Dynamics of Small Molecules: Experimental and Computational Studies Using Carbonyl Vibrational Modes as Probe

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SOLVATION STRUCTURES AND DYNAMICS OF SMALL MOLECULES: EXPERIMENTAL AND COMPUTATIONAL STUDIES USING CARBONYL VIBRATIONAL MODES AS PROBE

A Dissertation

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# TABLE OF CONTENTS

ACKNOWLEDGEMENTS........................................................................................................ii

ABSTRACT..........................................................................................................................v

CHAPTER 1: INTRODUCTION.................................................................................................1
  1.1 Background..................................................................................................................1
  1.2 Previous studies..........................................................................................................3
  1.3 Outline of this thesis..................................................................................................13
  1.4 References................................................................................................................15

CHAPTER 2: LINEAR AND NONLINEAR INFRARED SPECTROSCOPY.........................28
  2.1 Light-matter interaction ............................................................................................28
  2.2 Vibrational lineshape and spectra signatures ............................................................43
  2.3 Implementation of 2DIR spectroscopy ......................................................................52
  2.4 Computational methods...........................................................................................56
  2.5 Conclusions ...............................................................................................................62
  2.6 References.................................................................................................................62

CHAPTER 3: ACETATE ION AND ITS INTERESTING SOLVATION SHELL STRUCTURE
  AND DYNAMICS .............................................................................................................64
  3.1 Introduction ...............................................................................................................64
  3.2 Experimental and theoretical methods .......................................................................67
  3.3 Results ......................................................................................................................72
  3.4 Discussion ................................................................................................................76
  3.5 Summary ..................................................................................................................93
  3.6 References.................................................................................................................94

CHAPTER 4: AN AB INITIO MOLECULAR DYNAMICS STUDY OF THE SOLVATION
  STRUCTURE AND ULTRAFAST DYNAMICS OF LITHIUM SALTS IN ORGANIC
  CARBONATES: A COMPARISON BETWEEN LINEAR AND CYCLIC
  CARBONATES ................................................................................................................101
  4.1 Introduction ..............................................................................................................101
  4.2 Theoretical methods ...............................................................................................106
  4.3 Results and discussions ...........................................................................................109
  4.4 Conclusions .............................................................................................................130
  4.5 References...............................................................................................................131

CHAPTER 5: MOLECULAR STRUCTURE OF A CONDUCTIVE AND “NON-IONIC”
  MIXTURE OF MOLECULAR SOLVENTS........................................................................137
  5.1 Introduction ..............................................................................................................137
  5.2 Experimental and theoretical methods .......................................................................140
  5.3 Results ......................................................................................................................142
  5.4 Discussions ..............................................................................................................146
ABSTRACT

Solutions are ubiquitous in both the global environment and the human body, and play a significant role in scientific research and industrial production. The structures and dynamics of solutions have been studied for centuries. However, conventional experimental methods, whose intrinsic measuring time is on the order of nanoseconds to microseconds, could not detect the fast dynamics taking place in the solution on the timescale of femto- and pico-second. In this dissertation, the ultrafast two-dimensional infrared (2DIR) spectroscopy was applied to characterize the structure and dynamics in three different types of solutions on the sub-picosecond timescale. Linear Fourier transform infrared spectroscopy (FTIR) and computational calculations were performed to confirm the interpretation of the microscopic framework. Firstly, the ion effect on water structural dynamic properties at high concentration was studied by looking into the solvation shell of acetate ion in D$_2$O and in 6M NaCl solution. The FTIR lineshape of the carboxylate asymmetric mode and a dynamics component extracted from 2DIR is not affected by the highly concentrated salts, which is proved to be a particularity of the acetate ion by a comparative study on the azide ion. *Ab initio* molecular dynamics (AIMD) simulations confirmed the experimental observations and linked the observed vibrational phenomenon to the thermal rotation of acetate methyl group (—CH$_3$). Secondly, ion solvation structure and dynamics in organic solvents were investigated. By AIMD and *ab initio* umbrella sampling (AIUS), the structure and dynamics of the lithium solvation shell in cyclic and in linear carbonates were compared. The intercalation of entire molecules into the first solvation shell of lithium is found in cyclic carbonate, which leads to a more rigid and more organized solvation structure in cyclic carbonate. Finally, a conductive neutral molecular mixture of acetic acid (HAc) and N-methylimidazole (C1Im) was characterized by both experimental and theoretical methods. The
broadband peaks in FTIR was assigned as delocalized proton stretching mode in HAc-C1Im complexes. AIMD simulation, DFT calculation, and NMR measurements confirmed the existence of proton delocalization in the hydrogen bond between HAc and C1Im.
CHAPTER 1
INTRODUCTION

1.1. Background

Solutions are ubiquitous in both the environment and the human body. The ocean, which covers more than 70% of the earth’s surface, is one of the most common aqueous salt solutions.[1] This large expanse of briny water has a salinity of around 35 parts per thousand on average, and the ions in seawater, e.g., chloride, sodium, magnesium, calcium, and organic carbon ions, maintain a similar proportion to each other even if the salinity is different.[2] The ocean not only nourishes the marine organisms and affects them via osmosis, temperature, and pH,[3-9] but also influences the climate, weather, and air quality of the whole biosphere via the interaction between the ocean and the atmosphere.[10, 11] For example, oceanic CO$_2$ storage is estimated to be 39000 gigatons C, which is 5 times as much as that in the atmosphere. In the past 200 years, the ocean has been absorbing 38% of anthropogenic emission of CO$_2$, decreasing the atmospheric CO$_2$ concentration, and slowing climate warming.[12, 13]

In the human body, most biological processes take place in solutions. The human adult body is composed of up to 60% water by weight, which exists both in the living cells as the intracellular fluid and out of the living cells as the extracellular fluid, maintaining a stable environment with relatively constant pH, osmosis, et cetera, for the metabolisms taking place.[14, 15] Moreover, solutions are also indispensable for transferring nutrients, oxygen, carbon dioxide, and waste. By investigating the solution structure and dynamics (e.g., protein folding and ion transport), we can gain a better understanding of biological processes such as digestion, nerve impulse, and blood properties.[16-18]
Solution chemistry also plays an important role in scientific research, as well as in industrial production. The applications include organic synthesis, enzyme catalysis, new battery production, and drug delivery. The significance of solutions is the result of the high chemical reaction rate in solution. The liquid phase, because of its fast diffusion constant compared with the solid phase and its high particle density compared with the gas phase, therefore results in a high particle collision rate, making solutions the most favored medium for chemical processes in nature, daily life, industry, and research. Moreover, the solvent may affect the reactivity by influencing the enthalpy and entropy of the transition state. In particular, the speed of the reaction can change by orders of magnitude when the solvent is changed.[19] The mechanism on how the reaction rate is influenced by the solvents is still being investigated.[20-23] To understand the origin of life, the process of metabolism, the changing of the global environment, and to improve the industrial production as well, solution properties have been widely investigated in the last century.

Experimental methods such as NMR, X-ray scattering, and Raman scattering have been applied to obtain the solvation structure of either ions or protein molecules, as well as the translational and orientational dynamics of solutes on the timescale slower than picosecond.[24-26] Motions on faster timescales are investigated mostly by molecular simulation, where the residence time of the solute, short-time dynamics of libration, and solvation free energy are calculated. Meanwhile, the solvation structures can be visualized via molecular simulation. [25, 27-29] However, the conventional experimental methodologies are not suitable to measure the fast dynamics in solution, since their intrinsic measuring time, which is on the order of nanoseconds to microseconds, is not compatible with the fast motions in the solution, which is usually on the timescale of femto- and picoseconds. Another problem is the conventional methods cannot distinguish the solvation shell dynamics from bulk dynamics.
The development of ultrafast femtosecond laser pulses and the application of ultrafast infrared spectroscopy allow scientists to measure solvation dynamics on the sub-picosecond timescale. The infrared region is investigated because it’s on-resonance with the vibrational modes of chemical bonds, which have enough spatial resolution and time resolution for detecting solution processes. Vibrational infrared probes have been used to distinguish structure and dynamics in the solvation shell from the bulk solvent. A good probe is required to have a high signal intensity and high sensitivity to the local environment while introducing very few disturbances to the original system. Several vibrational infrared modes have been tested and proved to be good probes to study changes in the local environment, such as the nitrile stretching mode [30-37] and O-H stretching mode.[38-45] Carbonyl modes, including C=O stretching, COO symmetric stretching, and COO asymmetric stretching were also shown to be good solvation shell probes.[46-55] All of these carbonyl modes have a relatively high absorption coefficient, a sharp absorption peak in the frequency range which seldom overlaps with other highly intense absorption, and a good sensitivity to the local environment from nearby atoms to surrounding molecules, which makes these probes increasingly popular in the spectroscopic field.[54, 56-58]

In this dissertation, C=O vibrational modes were applied as a reliable probe to detect the solvation structure and dynamics of different kinds of solutions.

1.2. Previous studies

1.2.1. Aqueous salt solution

Water structure and dynamics have been widely investigated via computational simulation and experimental methods.[59-75] The dynamics of the hydrogen bond network has been found to occur over a range of time scales, where the slowest component is assigned to the randomization of the network through concerted hydrogen bond making and breaking rearrangements on the
timescale of 1.7 ps. On the other hand, the fastest component on the time scale of tens of femtosecond is interpreted in different ways, e.g., diffusive changes in the O–H · · · O hydrogen-bond distance or inertial motion.[70, 76, 77] Noteworthy, the orientation relaxation at a time scale of 2.6 ps is also associated with hydrogen bond network rearrangement.[68, 70]

The addition of ions into water leads to dramatic changes in its structural and dynamical properties. Studies on this topic date back to more than 100 years, when Hofmeister proposed the Hofmeister series describing the effects of different salts on protein solubility.[78] Over the last few decades, the structure of the ion solvation shell, e.g., coordination number, mean distances, and spatial configuration, has been revealed via numerous methodologies, including X-ray diffraction, neutron diffraction, EXAFS spectroscopy, XANES spectroscopy, Raman spectroscopy, infrared spectroscopy, NMR relaxation, dielectric relaxation, Rayleigh scattering, Brillouin scattering, and molecular dynamics.[24-26, 79] Most scientists believe that ions have influences on the water structure outside of the ion solvation shell. These long-range influences could be either enhancing ("structure-maker") or destroying ("structure-breaker") the tetrahedral structure of the water hydrogen bond network.[26] Although some researchers claimed that the long-range structuring due to the presence of ions does not exist,[80] the structure making and breaking effect of ions in water or biological systems is still being widely studied.[24, 81] In fact, dynamics of the aqueous salt solutions have been investigated for decades via NMR, Rayleigh scattering, etc. at timescales slower than a few picoseconds, until a breakthrough has been made in the past 40 years with the application of ultrafast spectroscopy technique, where the ultrafast aqueous solution dynamics on the timescale of pico- and femtoseconds are detected with ultrafast infrared laser pulses.[25, 59, 82-87] [88, 89]
Ion effects on water structure and dynamics properties and protein folding are concentration-dependent. At very low concentrations (< 0.1 M), electrostatics is dominant compared with specific ion effects. Almost all the studies focus on the intermediate concentration (0.1-2.0 M), where a large amount of solvation shell structures and bulk water exist simultaneously. However, the structural and dynamical properties of aqueous ion solutions at very high concentrations (> 2 M) are scarcely investigated, where all the water molecules are captured by an ion hydration shell, and all the ions “salt out” the proteins.[90]

To fill this gap, a system composed of sodium acetate (CH₃COONa) solvated by water with 6 M sodium chloride (NaCl) is investigated in this dissertation (Figure 1.1). The questions of significance remained now are: how does the hydration dynamics of an acetate ion in the vicinity of highly-concentrated salt ions differ from those in pure water; what is the structure of the acetate ion solvation shell; and how is the long-range structuring and interactions? Noticeable, the speciation of the acetate ion in the 6 M NaCl solution is of interest. Infrared and Raman study of the acetate ion in the C-C vibrational region revealed that the acetate forms contact ion pairs with neither sodium nor alkaline-earth ions.[91] A molecular simulation study explained the lack of ion pair formation by thermodynamics, herein the contact ion pair of acetate was found to be of entropic origin, while the solvent-shared ion pair was mainly enthalpically favorable.[92] Therefore, the molecular mechanism behind the lack of contact ion pair formation by the acetate ion is investigated here.
Figure 1.1. Acetate ion solvated in water (left), and acetate ion solvated in 6 M sodium chloride aqueous solution (right). Molecules shown in the ball-and-stick model are acetate ion; molecules in the licorice drawing method are water molecules. The dispersed green and blue balls represent Cl\(^-\) and Na\(^+\) ions respectively.

1.2.2. **Ions in organic solvent systems**

Ions in organic solvent systems have attracted attention in the last few decades. One interest is the ion transfer from water to organic solvents, which is important in ion extraction, membrane transport, and electrode selectivity.[93-96] The Gibbs free energy profile and further structural properties of the process with either monoatomic ions such as F\(^-\), Cl\(^-\), and Li\(^+\), or polyatomic ions such as Me\(_4\)N\(^+\), SCN\(^-\), and ClO\(_4\)\(^-\) have been obtained experimentally and theoretically.[97-109] These studies reveal the co-extraction of water molecules when transferring ions through the interface, which means the ions do not exist as bare ions in the organic solution but as ion water clusters. Solvation shell components of various ions are investigated, while interactions between ion and hydrated water; ion and the rest solvent molecules; along with hydration shell and organic solvents are demonstrated to be important in determining the solvation shell structural dynamics.

Another popular topic in organic solvents is the solvent effects on chemical reactions taking place in solution. Kinetics, production yield, and selectivity of reactions can be tuned by modifying
the organic solvents. It is found that the rate constant of CH₃I and Cl⁻ displacement reaction is increased by up to 6 orders of magnitude when changing the solvent from MeOH to DMF. Similar dramatic changes in reaction rate constants are observed in many other chemical reactions. [110] It is found that weak solvation of anion or cation reactants and strong solvation of activated complexes leads to a high reaction rate constant.[111] Solvent effects have also been observed on product yield of organic synthesis.[112] In addition, it was found that the choice of organic solvent has a remarkable effect on the stereoselectivity and enantioselectivity, enhancing the proportion of either cis- or trans-isomers, and controlling the product chirality in organic synthesis.[113, 114] Efforts have been made to understand the mechanism behind this organic solvent effect. Solute-solvent interactions and solute-solute interactions are investigated in different organic solvents, as a result, the importance of ion pairing was found.[115] The ions are divided into different categories: free ions (FI), solvent separated ion pairs (SSIP), contact ion pairs (CIP), and aggregates (AGG).[116-120] The formation of ion pairs is influenced by the polarity of the solvents. In polar solvents, SSIP and FI are energetically favored, while in nonpolar solvent, CIP is energetically favorable.[121] Ion pairs are believed to change the reaction path, where the CIP is believed to control the selectivity of the reaction.[111, 114]

One more typical example of metal-organic coordination systems is the lithium-ion battery (LIB). A commercial LIB is mainly composed of lithium-ion and linear and cyclic carbonates.[122] The interest in lithium-ion batteries comes from the growing global demand for portable energy storage devices, as well as the advantages of LIB such as low cost, high energy density, and no memory effect.[122-124] There are numerous studies focusing on improvement of the LIB performance, by investigating substitutes on: cation, e.g., Na⁺; anion, e.g., PF₆⁻, AsF₆⁻,
BF₄-, and TFSI-; and organic solvents, e.g., carbonates and ethers.[125] However, experimental and theoretical studies have produced conflicting results in structural and dynamical analysis.

The coordination number of lithium ions investigated by ultrafast spectroscopic studies, Raman, and FTIR spectroscopy, is found to be 4 in some studies, differing from 2 or 6 in other studies.[126-132] The controversies also appear in computational studies.[118, 133-148] The implications will be discussed further in chapter four.

The ionic speciation of lithium ions and its counterion in solutions of organic carbonates is also an unsolved problem.[117, 128, 132, 149] Formation of ion pairs and aggregation, wherein the solvent molecules do not solvate the solute completely, decreases the activity coefficient of free ions. Since free ions act as charge carriers in battery solution, the formation of ion pairs and aggregation leads to low conductivity and capacity of the lithium-ion battery. [150] Experimental studies using infrared spectroscopy have obtained different results on ion speciation. An ultrafast vibrational study on the orientational correlation time of C=O stretching mode demonstrated that all lithium ions form contact ion pairs (CIP) with common counterions, i.e., PF₆-, BF₄-, and ClO₄-, in a cyclic carbonate, i.e., ethylene carbonate (EC), at concentrations higher than 0.5 M.[128] However, other studies using the same method focusing on the same vibrational mode pointed out that at those concentrations, the predominant ion species are FI and CIP in cyclic carbonate and FI and SSIP in linear carbonate.[117, 126] Similarly, computational calculations also showed inconsistencies. Classical MD indicated a large population of CIP existing in lithium hexafluorophosphate solutions of EC.[146] In contrast, the potential energy surface for the lithium tetrafluoroborate in EC at CAM-B3LYP/6-31G(d) level suggested that SSIPs are the most energetically favorable species.[143] Moreover, another study using the energy representation method for LiBF₄ and LiPF₆ in both propylene carbonate (PC) and dimethyl carbonate (DMC)
claimed that CIP is the most energetically favorable species irrespective of the dielectric constant of the carbonate.[147]

Debates also focus on the rate of the solvent exchange process. The mobility of lithium ion is a determining factor in battery performance since the ion mobility in solutions is much slower than the electron mobility in the wire as a charge carrier. Microscopic fluxional solvent exchange processes are important in understanding the macroscopic battery property of lithium ion mobility. The mobility of the lithium ion is mainly determined by the properties of the solvent molecules, which affects the diffusion of the lithium ion by the solvent-solute interactions and the solvent-solvent interactions.[122, 125] Although the solvent-solute interactions between the lithium ion and either the cyclic or linear carbonates have been investigated through the viewpoint of the equilibrium structure, still the picture of the solute-solvent dynamics is not clear.[132, 151-158] The competition between the entropically favored linear carbonates and the enthalpically favored cyclic carbonates demands the understanding of solvent exchange dynamics in different carbonate solutions.[159] In this case, ultrafast infrared spectroscopy has been applied for its sensitivity and time resolution. (See in Chapter 2) However, previous ultrafast spectroscopies resulted in controversies. Minhaeng Cho and his group predicted a fast solvent exchange between the lithium ion and linear carbonate in both single solvent and co-solvent systems. Here, both the formation and dissociation processes of Li+---carbonate complex is on the timescale of less than 5 ps.[129, 160] On the other hand, another study pointed out that the experimental signature assigned to solvent exchange arises from a vibrational energy transfer mechanism due to deformations of the solvation shell of the lithium ion.[126]
In this project, systems of LiPF$_6$ solvated in cyclic carbonate and linear carbonate (Figure 1.2) will be investigated by *ab initio* molecular dynamics and umbrella sampling to illustrate the coordination number, ion speciation, and solvent exchange rate in the solution.

Figure 1.2. LiPF$_6$ solvated in cyclic (butylene carbonate, left), and linear (dimethyl carbonate, right) carbonates. The brown ball at the center of the box represents Li+, while the green balls in octahedron shape represent PF$_6$- ion, and the carbonates are represented by lines.

**1.2.3. Neutral molecular mixture**

Liquid phase solutions can be simply divided into three categories: ions solvated by neutral molecules, mixtures of neutral species, and mixtures of ions, namely ionic liquids. Systems discussed in Section 1.2.1 and 1.2.2 are in the first category, and the second category will be introduced in this section. The study of a solution containing two neutral organic species appealed to an increasing number of scientists because of its unique conductivity behavior: the equimolar mixture of acetic acid (HAc) and N-methylimidazole (C$_1$Im) was found to have a conductivity 4 orders of magnitude higher than neat HAc and 2 orders of magnitude higher than C$_1$Im (shown in Figure 1.3), while the mixture was found to be composed of only the electronically neutral molecular species.[161-166] The Grotthuss mechanism was then proposed to be the main mechanism for the conductive property of the neutral molecular mixture and was investigated by
both experiments and computational simulation,[165, 167] leading to a desire for understanding the microscopic structure of hydrogen-bond network, as well as the proton motions related to the conductivity behavior.

Regarding the solution structure, there is a debate about whether the system is composed of neutral molecules, acid and base ions, or the complexes formed by base and acid molecules. As mentioned before, the HAc and C₁Im mixture was found to have a conductivity 4 orders of magnitude higher than its neat acid and 2 orders of magnitude higher than its neat base, which is often related to a protic ionic liquid, especially when the system is composed of a Brønsted acid and a Brønsted base. This assumption is in agreement with previous NMR studies, where the ionicity of the equimolar mixture is found to be 92.8% by concentration-dependent NMR experiment, and both the proton transfer enthalpy and entropy are found to be 9.33 kJ/mol, and 11.29 J·(mol·K)⁻¹ respectively by temperature-dependent NMR studies.[168] However, Raman spectroscopy by Umebayashi group on the frequency range of C=C and C=O vibration absorption showed that electrically neutral molecular species predominantly exist in the equimolar mixture.[161] This result also agrees with the fact that ΔpKa value between HAc and C₁Im is as small as 2.4, which means the proton transfer is incomplete and the solution is characterized as a poor ionic liquid.[161, 169-171]

Meanwhile, the Umebayashi group calculated the energy difference between molecular complexes and their corresponding conjugated ion structures. The conjugated [Ac]⁻ -- [C₁hIm]⁺ state has ~7 kJ/mol higher free energy compared with the molecular complexes by PCM calculations using acetonitrile as a medium.[161] According to the Bell–Evans–Polanyi principle,[172, 173] their group considered the activation energy of the proton transfer process to be small, which is comparable with thermal energy at room temperature, indicating fast proton
transfer and reorientation of the surrounding neutral molecules.[161] This fast proton transfer leads to the breakout finding of the Grutthuss mechanism from not only the *ab initio* molecular dynamics (AIMD) simulation, but also the spectroscopy signatures of Raman, X-ray scattering, and NMR, which can explain the high conductivity in the neutral molecular system.[165, 167] The AIMD calculation obtained the fraction of neutral molecules to be 75-80% in the equimolar mixture,[165] which is in agreement with the results of Raman measurements. Moreover, measurements of different molar ratios of this HAc/C\textsubscript{1}Im mixture have been applied to obtain the conductivity curve, and two electrical conductivity maxima were found, at x(HAc)=0.65 and x(HAc)=0.85 respectively.[163, 164] This two-maximum conductivity curve indicates a more intricate picture wherein the speciation may change with the molar ratio of the mixture. Furthermore, there is another question about the assignment of the broadband peak in infrared spectroscopy on the frequency range of 1800 cm\textsuperscript{-1} to 3000 cm\textsuperscript{-1}, which is not shown in Umebayashi’s paper.

Figure 1.3. Acetic acid and N-methylimidazole molecular mixture. The red, green, blue, and white colors represent oxygen, carbon, nitrogen, and hydrogen atom respectively.
As a result, problems remain in this system: Is it composed of ions, neutral species, or neither of them; what are the structures of the complexes; how do they change with HAc concentration; and which conformers of the complexes are responsible for conductive behavior?

1.3. Outline of this thesis

The objective of the work described in this thesis is to investigate the solvation structure and dynamics of small molecule solutions with C=O stretch mode as a probe using FTIR and 2DIR spectroscopy assisted with molecular dynamics simulation. In chapter 2, the theory of third-order nonlinear response, the ultrafast pulse generation, and the 2DIR experiment setup are described. Then, the interpretation of spectral signature of 2DIR, like the spectral diffusion and the crosspeak, is introduced.

In chapter 3, the solvation dynamics of sodium acetate in water and in 6 M sodium chloride solution is investigated by linear and two-dimensional infrared spectroscopies using the carboxylate asymmetric stretch mode of the acetate ion as a probe. The linear IR spectra showed that the carboxylate asymmetric stretch central frequency and bandwidth are not significantly perturbed by the presence of a large amount of sodium chloride. Then, the frequency-frequency autocorrelation functions (FFCF) extracted from the time evolution of 2DIR spectra revealed that a dynamical component having a picosecond time constant is also not affected by the presence of high salt concentrations. Next, the asymmetric stretch of the azide ion in both the pure water and a highly-concentrated salt solution was investigated by linear infrared and 2DIR spectroscopies as a contrast. Finally, ab initio molecular dynamics simulations and a frequency map are calculated to confirm experimental observations and linked the observed vibrational phenomenon to the hydrogen bond structure and dynamics of the acetate first solvation shell, which is governed by the thermal rotation of its methyl group (–CH3).
In Chapter 4, the solvation shell structure and dynamics of lithium ion in linear and cyclic carbonates are investigated by *ab initio* molecular dynamics (AIMD) simulation and *ab initio* umbrella sampling (AIUS). The solvation shell structures in each carbonate solvent were characterized by radial distribution function between lithium ion and either the oxygen or the carbon of the carbonyl, demonstrating that the molecular arrangement of the carbonates directly coordinating Li$^+$ is not significantly altered by the carbonate chemical nature. The ion speciation was then investigated via radial distribution function between Li$^+$ and PF$_6^-$ and potential of mean force obtained from AIMD, showing significantly different pictures between cyclic and linear carbonates, which could be associated with the intercalation phenomenon observed in cyclic carbonates. In addition, the solvation shell dynamics was interrogated by the autocorrelation function of the structure factor in each frame. Finally, the solvent exchange process with a transition state was studied by AIUS and AIMD, revealing the dynamics of the geometrical changes of the carbonates solvating Li$^+$ at the timescale of tenths of picoseconds, while the ion pairing and solvent chemical exchange processes were found to be at time scales at least an order of magnitude larger than tenth.

In Chapter 5, FTIR, 2DIR, and AIMD simulation are applied to investigate the structure of a mixture composed of acetic acid and N-methylimidazole. Conductivities and viscosities of the mixture at different molar ratios were measured by a conductivity meter and a viscometer. Broadband FTIR absorption centered at ~1800 cm$^{-1}$ and ~2500 cm$^{-1}$ was observed over a large range of HAc molar fractions (0.05-0.97), which is an evidence of delocalized protons. Concentrate-dependent AIMD simulations indicated the existence of delocalized protons and revealed that there are two kinds of complexes existing in solution. One is formed by HAc with several C$_1$Im and is the dominant species at low x(HAc); the other is C$_1$Im with several HAc and
is the dominant species at high x(HAc). DFT calculations of representative structures taken from AIMD simulation confirmed the existence of the delocalized proton. Finally, the flat-bottom potential energy surface determined from DFT calculation and pump-probe spectra finally confirmed the proton delocalization existence in both complexes.

1.4. References


2.1. Light-matter interactions

In molecular spectroscopy, photons are used to investigate the matter through light-matter interactions. Albeit the molecules cannot be observed directly through this method, information on molecular structure and dynamics is obtained from analyzing the detected spectra. To extract microscopic information in spectroscopy, a quantitative formalism of the light-matter interaction process is required. For this purpose, following the description popularized by Mukamel, Boyd, and Cho, a semi-classical treatment is applied, which means the material system is described quantum mechanically, while the time-dependent electromagnetic field is treated classically.[1-3]

2.1.1. Time-dependent Schrödinger equation

One of the most simplified models for a molecule interacting with a photon consists of a single molecule system that can be described by a single wavefunction, which is defined as a pure state, and an external electric field. The time-dependent Hamiltonian of an isolated vibrator is expressed as:

\[ \hat{H}(t) = \hat{H}_0 + \hat{W}(t) \]  \hspace{1cm} (1)

where \( \hat{H}_0 \) is the Hamiltonian for the isolated molecule, and \( \hat{W}(t) \) is the quantum mechanical operator for the interaction energy generated by the external time-dependent electromagnetic field and the dipole moment of the molecule. The interaction energy \( \hat{W}(t) \) then is described as

\[ \hat{W}(t) = -\vec{\mu} \cdot \vec{E}(t) \]  \hspace{1cm} (2)

where \( \vec{\mu} \) is the molecule’s dipole moment and \( \vec{E}(t) \) is the external time-dependent electromagnetic field. Consider the electromagnetic field simply as
\[ E(t) = E'(t) \cos(\omega t) \quad (3) \]

where \( E'(t) \) is the time-dependent amplitude.

The time-evolution of the molecular state is given by solving the time-dependent Schrödinger equation:

\[ \frac{\partial}{\partial t} |\psi(t)\rangle = - \frac{i}{\hbar} \hat{H}(t) |\psi(t)\rangle. \quad (4) \]

When the external electric field \( \hat{W}(t) \) is much smaller than the internal field \( \hat{H}_0 \), the external field exerted on the molecule can only disturb the coefficients of the wavefunctions, but not the eigenstates themselves. As a result, the wavefunction \( \psi(t) \) can be expanded with the eigenstates of the isolated molecule Hamiltonian \( \hat{H}_0 \) as a basis:

\[ |\psi(t)\rangle = \sum_n c_n(t) |n\rangle, \quad (5) \]

where \( c_n(t) \) is the time dependent probability coefficient, and

\[ \hat{H}_0 |n\rangle = E_n |n\rangle. \quad (6) \]

Substitute equation (6) into equation (4):

\[ \frac{\partial}{\partial t} c_m(t) = - \frac{i}{\hbar} \sum_n H_{mn} c_n(t), \quad (7) \]

where \( H_{mn} = \langle m | \hat{H}(t) | n \rangle \).
2.1.2. Density matrix of pure state and Liouville–von Neumann equation

The matrix $\| H \|$ above is another way of representing a quantum operator. With a well-defined orthogonal wavefunction basis set, operator $\hat{A}$ can be represented by a matrix with the matrix elements defined by:

$$ A_{mn} = \langle m | \hat{A} | n \rangle. \quad (8) $$

The density matrix is an operator to describe self-interaction, defined as the outer product of a wavefunction and its complex conjugate:

$$ \rho \equiv |\psi\rangle\langle\psi|, \quad (9) $$

with $\rho_{mn} = \langle m | \psi \rangle \langle \psi | n \rangle = c_m c_n^*$. In infrared spectroscopy, the states with most measurable population are $|0\rangle$ and $|1\rangle$. Consider a system in which only those two states can be accessed by the laser pulse. After a laser pulse, according to Equation (5), the system is in a superposition of $|0\rangle$ and $|1\rangle$:

$$ |\psi_{01}(t)\rangle = c_0(t)|0\rangle + c_1(t)|1\rangle $$

$$ = c_0 e^{-iE_0 t / \hbar} |0\rangle + c_1 e^{-iE_1 t / \hbar} |1\rangle. \quad (10) $$

$$ \rho = |\psi_{01}\rangle\langle\psi_{01}| = \begin{pmatrix} c_0(t) c_0^*(t) & c_0(t) c_1^*(t) \\ c_1(t) c_0^*(t) & c_1(t) c_1^*(t) \end{pmatrix} $$

$$ = \begin{pmatrix} c_0^2 & c_0 c_1^* e^{i\omega_{01} t} \\ c_1 c_0^* e^{-i\omega_{01} t} & c_1^2 \end{pmatrix}, \quad (11) $$

where $\omega_{01}$ is the angular frequency that is corresponding to the energy difference between ground state $|0\rangle$ and first excited state $|1\rangle$. 
The diagonal terms of $\| \rho \|$ correspond to the probability of the system being in a certain basis set state, and the sum of them is 1 when the wavefunction $|\psi\rangle$ is normalized. The off-diagonal terms are coherence, which is the oscillatory process that interacts with the external field and emits a field.

When the density matrix is a diagonal matrix, the system described by the wavefunction $|\psi\rangle$ is in a *population state*. In the case of a pure state, a population state can only be a system composed of a single basis set (eigenstate/eigenfunction). When the off-diagonal terms in the density matrix are not all zero, the system is in a *coherent state*.

With a density matrix, the expectation of an operator $\hat{A}$ can be easily written as:

$$\langle \hat{A} \rangle = \langle \psi(t) | \hat{A} | \psi(t) \rangle = \sum_{mn} \rho_{nm} A_{mn} = Tr(\rho(t) \hat{A}) \equiv \langle \rho(t) \hat{A} \rangle, \quad (12)$$

and the time evolution of the density matrix is:

$$\frac{d}{dt} \rho(t) = -\frac{i}{\hbar} \hat{H}(t) \rho(t) + \frac{i}{\hbar} \rho(t) \hat{H}(t) = -\frac{i}{\hbar} [\hat{H}(t), \rho(t)], \quad (13)$$

which is the *Liouville-von Neumann* equation.

So far, with the application of matrix in the field of quantum mechanics, the eigenstate, the wavefunction, and the operator can be represented as basis set, vector, and matrix respectively. As a result, the complicated integral calculation is transferred into simple matrix operation. The other advantage of using density matrix will be introduced in the next section.
2.1.3. Molecular ensemble and dephasing

An isolated molecule model is not sufficient to describe the real light-matter interaction in condensed phase. In condensed phase, the vibrational frequency and quantum states are slightly distinct from molecule to molecule because of the different surrounding environment they experience and different spatial structures they have. Therefore, a statistical treatment is required, and the density matrix again shows its convenience in describing a molecular ensemble. Density matrix of an ensemble is defined as:

$$\rho = \sum_s p_s |\psi_s\rangle\langle\psi_s|$$

where $p_s$ is the probability of the state $|\psi_s\rangle$ in the ensemble, and $\sum_s p_s = 1$. Density matrix of an ensemble also fulfills the Liouville-von Neumann equation.

In $|0\rangle$ and $|1\rangle$ two states system, after substitution Equation (11) into Equation (14), the density matrix of ensemble after a laser pulse is:

$$\rho = \sum_s p_s |\psi_s\rangle\langle\psi_s| = \begin{pmatrix} \langle c_0(t)c_0^*(t) \rangle & \langle c_0(t)c_1^*(t) \rangle \\ \langle c_1(t)c_0^*(t) \rangle & \langle c_1(t)c_1^*(t) \rangle \end{pmatrix}$$

$$= \begin{pmatrix} \langle c_0^2 \rangle & \langle c_0 c_1 e^{i\omega_0 t} \rangle \\ \langle c_1 c_0 e^{-i\omega_0 t} \rangle & \langle c_1^2 \rangle \end{pmatrix}.$$  \hspace{1cm} \text{(15)}

The symbol $\langle ... \rangle$ here represents ensemble average.

As time evolves, systems in the excited state $|1\rangle$ move to the ground state $|0\rangle$, which is the vibrational population relaxation. The vibrational relaxation results in a decay of $|1\rangle$ state population $\rho_{11}$ with time constant $T_1$ along with an increasing of $|0\rangle$ state population $\rho_{00}$:
\[ \rho_{11}(t) = \rho_{11}(0)e^{-t/T_1}, \]  
\[ \rho_{00}(t) = 1 - \rho_{11}(t). \]  

The *homogeneous dephasing* is a decay in the off-diagonal terms of the density matrix, characterized with a homogeneous dephasing time \( T_2 \):

\[ \rho_{01}(t) = c_0 c_1^* e^{i\omega_{01}t} e^{-t/T_2}, \]  
\[ \rho_{10}(t) = c_1 c_0^* e^{-i\omega_{01}t} e^{-t/T_2}. \]  

\( T_1 \) contributes to \( T_2 \) through the decrease of off-diagonal elements. The relationship between \( T_1 \) and \( T_2 \) is described as:

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

where \( T_2^* \) is the pure dephasing.

### 2.1.4. Perturbation theory

To separate the time propagation caused by external electric field and that intrinsic to the molecule itself, the wavefunction \(|\psi(t)\rangle\) can be written in the form of the *interaction picture*:

\[ |\psi(t)\rangle \equiv e^{-\frac{i}{\hbar}\tilde{H}_0(t-t_0)}|\psi_I(t)\rangle \]  

where \( e^{-\frac{i}{\hbar}\tilde{H}_0(t-t_0)} \) is the time evolution component under the effect of intrinsic Hamiltonian \( \tilde{H}_0 \) for the isolated molecule, and the time propagation caused by a laser pulse is described by \(|\psi_I(t)\rangle\). \(|\psi(t)\rangle\) represents an ensemble density matrix.

The time evolution of \(|\psi_I(t)\rangle\) can be written in a similar form to the Schrodinger equation, thus the Liouville-von Neumann equation is valid for \(|\psi_I(t)\rangle\):
\[
\frac{\partial}{\partial t} |\psi_t(t)\rangle = -i \hbar \tilde{W}_I(t) |\psi_t(t)\rangle \tag{22}
\]

where \(\tilde{W}_I(t)\) is defined as:

\[
\tilde{W}_I(t) \equiv e^{i \hbar \tilde{H}_0(t-t_0)} \tilde{W}(t_0) e^{-i \hbar \tilde{H}_0(t-t_0)}. \tag{23}
\]

Substitute Eq. (21), Eq. (22) and Eq. (23) to the definition of density matrix, then the density matrix described in interaction picture is:

\[
|\psi(t)\rangle \langle \psi(t)| = e^{-i \hbar \tilde{H}_0(t-t_0)} |\psi_I(t)\rangle \langle \psi_I(t)| e^{i \hbar \tilde{H}_0(t-t_0)}. \tag{24}
\]

Or written as:

\[
\rho(t) = e^{-i \hbar \tilde{H}_0(t-t_0)} \rho_I(t) e^{i \hbar \tilde{H}_0(t-t_0)}. \tag{25}
\]

\(\rho_I(t)\) also fulfills the Liouville-von Neumann equation:

\[
\frac{d}{dt} \rho_I(t) = -i \hbar [\tilde{W}_I(t), \rho_I(t)]. \tag{26}
\]

Thus, the perturbative expansion of \(\rho_I(t)\) is:

\[
\rho_I(t) = \rho_I(t_0) + \sum_{n=1}^{\infty} \left( -\frac{i}{\hbar} \right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} ... \int_{t_0}^{\tau_2} d\tau_1 \left[ [\tilde{W}_I(\tau_n), [\tilde{W}_I(\tau_{n-1}), ... [\tilde{W}_I(\tau_1), \rho_I(t_0)] ... ] \right]. \tag{27}
\]

Go back to the density matrix under the full Hamiltonian \(\rho(t)\):

\[
\rho(t) = \rho(t_0) + \sum_{n=1}^{\infty} \left( -\frac{i}{\hbar} \right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} ... \int_{t_0}^{\tau_2} d\tau_1 \left[ [\tilde{W}_I(\tau_n), [\tilde{W}_I(\tau_{n-1}), ... [\tilde{W}_I(\tau_1), \rho(t_0)] ... ] \right] e^{-i \hbar \tilde{H}_0(t-t_0)} e^{i \hbar \tilde{H}_0(t-t_0)}. \tag{28}
\]
Substitute Equation (2) into Equation (28):
\[
\rho(t) = \rho(t_0) + \sum_{n=1}^{\infty} \left( -\frac{i}{\hbar} \right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} ... \int_{t_0}^{\tau_2} d\tau_1 E(\tau_n)E(\tau_{n-1}) ... E(t_0) \\
\left[ \mu(\tau_n), [\mu(\tau_{n-1}), ... [\mu(\tau_1), \rho(t_0)] ... ] \right] e^{i\hbar H_0(t-t_0)},
\]

Where
\[
\hat{\mu}_I(t) \equiv e^{\frac{i}{\hbar} H_0(t-t_0)} \hat{\mu}(t_0) e^{-\frac{i}{\hbar} H_0(t-t_0)}.
\]

In the following part, the subscript \( I \) of interaction picture is discarded. The Schrödinger picture and the interaction picture are distinguished by \( \hat{\mu} \) and \( \hat{\mu}(t) \), since the former is time-independent and the latter is time-dependent.

2.1.5. Nonlinear polarization and response function

In the picture of linear and nonlinear spectroscopy, the macroscopic polarization is a significant bridge between the incident photon and the signal photon. It is induced by the external electromagnetic field, and radiates the signal electromagnetic field.

The perturbative expansion of the macroscopic polarization is:
\[
\bar{P}(t) = p^{(0)} + p^{(1)} + p^{(2)} + p^{(3)} + ..., \quad (31)
\]
where \( p^{(n)} \) is the nth-order polarization resulting from n incident fields.

The ensemble average of \( P(t) \) can be obtained from the density matrix as:
\[
\bar{P}(t) = Tr(\hat{\mu} \rho(t)) = Tr(\hat{\mu} \rho^{(0)}(t)) + Tr(\hat{\mu} \rho^{(1)}(t)) \\
+ Tr(\hat{\mu} \rho^{(2)}(t)) + ...
\]

Substitute Equation (29) into Equation (32):
\[ \bar{P}^{(n)}(t) = Tr \left( \hat{\mu} \rho^{(n)}(t) \right) = \langle \hat{\mu} \rho^{(n)}(t) \rangle \]

\[
= - \left( -\frac{i}{\hbar} \right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 E(\tau_n)E(\tau_{n-1}) \cdots E(\tau_1) \]

(33)

\[
\langle \hat{\mu}(t)[\hat{\mu}(\tau_n), [\hat{\mu}(\tau_{n-1}), \ldots [\hat{\mu}(\tau_1), \rho(t_0)] \ldots ] \rangle.
\]

Assume \( \rho(t_0) \) is the time-independent density matrix under the internal Hamiltonian \( \hat{H}_0 \), so send \( t_0 \to -\infty \). Set \( \tau_1 = 0 \), and use the time interval \( t \) instead of absolute time \( \tau \):

\[
t_1 = \tau_2 - \tau_1 \\
t_2 = \tau_3 - \tau_2 \\
\ldots \ldots \\
t_n = \tau - \tau_n
\]

(34)

The nth-order polarization can be written as the convolution of n incident fields and an nth-order response function \( R^{(n)} \):

\[
\bar{P}^{(n)}(t) = \int_{0}^{\infty} dt_n \int_{0}^{\infty} dt_{n-1} \cdots \int_{0}^{\infty} dt_1 E(t - t_n)E(t - t_n - t_{n-1}) \cdots E(t - t_n - t_{n-1} - \cdots - t_1)R^{(n)}(t_n, \ldots, t_1),
\]

(35)

where the response function \( R^{(n)} \) is described as:

\[
R^{(n)}(t_n, \ldots, t_1) =
\]

\[
-(-\frac{i}{\hbar})^n \langle \hat{\mu}(t_n + \cdots + t_1)[\hat{\mu}(t_{n-1} + \cdots + t_1), \ldots, [\hat{\mu}(0), \rho(-\infty)] \ldots ] \rangle
\]

(36)

In the linear spectroscopy, where n=1, the macroscopic polarization is describes as:
\[ P^{(1)}(t) = \int_{0}^{\infty} dt_{1} E(t - t_{1}) R^{(1)}(t_{1}), \]  
(37)

where

\[ R^{(1)}(t_{1}) = \frac{i}{\hbar} \langle \hat{\mu}(t_{1}) | [\hat{\mu}(0), \rho(-\infty)] \rangle. \]  
(38)

The relationship between macroscopic polarization and emitted light is described as:

\[ E_{\text{sig}}(t) = iP(t). \]  
(39)

Substitute Equation (39) and Equation (38) to Equation (37), an opposite sign between incident electric field \( E(t) \) and emitted signal \( E_{\text{sig}}(t) \) is obtained. This destructive inference between emitted light and incident light causes the decrease of optical density of light after the sample, which is described as the absorption process in linear spectroscopy.

In third-order nonlinear spectroscopy, the third-order polarization generated by three external electromagnetic fields is described as:

\[ \overline{P}^{(3)}(t) = \int_{0}^{\infty} dt_{1} \int_{0}^{\infty} dt_{2} \int_{0}^{\infty} dt_{3} E(t - t_{3}) E(t - t_{3} - t_{2}) E(t - t_{3} - t_{2} - t_{1}) R^{(3)}(t_{1}, t_{2}, t_{3}), \]  
(40)

Where

\[ R^{(3)}(t_{1}, t_{2}, t_{3}) = \left( \frac{i}{\hbar} \right)^{3} \langle \hat{\mu}(t_{1} + t_{2} + t_{3}) [\hat{\mu}(t_{1} + t_{2}), \hat{\mu}(t_{3}), [\hat{\mu}(0), \rho(-\infty)] \rangle \]  
(41)
2.1.6. Rotating wave approximation and Feynman diagrams

In the previous part, the macroscopic polarization is derived with a simplified description of electric field $E(t)$. Here, a more sophisticated description of the electric field is taken as a real sine or cosine function, which can be written as the summation of a pair of complex conjugates:

$$E_0(t) = 2E'(t)\cos(\theta) = E'(t)(e^{-i\omega t} + e^{+i\omega t}) = E(t) + E^*(t), \quad (42)$$

where $E'(t)$ is the amplitude. Take the linear interaction for instance, the convolution of the electric field and molecular response can be rewritten as:

$$\overline{P}^{(1)}(t) = \int_0^\infty dt_1 [E(t - t_1) + E^*(t - t_1)]R^{(1)}(t_1)$$

$$= \frac{i}{\hbar} \int_0^\infty dt_1 \{E(t - t_1)(\bar{\mu}(t_1)\bar{\mu}(0))\rho(-\infty))$$

$$+ \frac{i}{\hbar} \int_0^\infty dt_1 E^*(t - t_1)(\bar{\mu}(t_1)\bar{\mu}(0))\rho(-\infty))$$

$$- \frac{i}{\hbar} \int_0^\infty dt_1 E^*(t - t_1)\rho(-\infty)\bar{\mu}(0)\bar{\mu}(t_1)\}$$

$$- \frac{i}{\hbar} \int_0^\infty dt_1 E(t - t_1)\rho(-\infty)\bar{\mu}(0)\bar{\mu}(t_1)).$$

Consider the dephasing between 0 and $t_1$:  

38
\[
\overline{p^{(1)}(t)} = \frac{i}{\hbar} \mu_{01}^2 e^{-i \omega t} \int_0^\infty dt_1 E'(t - t_1) e^{-t_1/T_2} + \frac{i}{\hbar} \mu_{01}^2 e^{i \omega t} \int_0^\infty dt_1 E'(t - t_1) e^{-t_1/T_2} e^{-2i \omega t}
\]

\[
- \frac{i}{\hbar} \mu_{01}^2 e^{i \omega t} \int_0^\infty dt_1 E'(t - t_1) e^{-t_1/T_2}
\]

\[
- \frac{i}{\hbar} \mu_{01}^2 e^{-i \omega t} \int_0^\infty dt_1 E'(t - t_1) e^{-t_1/T_2} e^{2i \omega t}.
\]

The second and fourth integral have a fast oscillating component \(e^{\pm 2i \omega t}\), causing the convolution average to 0 over time. Therefore, compared with the first and third integral, the second and the fourth can be neglected. This is the rotating wave approximation, and it reduces the number of convolutions that need to be considered by half:

\[
\overline{p^{(1)}(t)} = \frac{i}{\hbar} \mu_{01}^2 e^{-i \omega t} \int_0^\infty dt_1 E'(t - t_1) e^{-t_1/T_2}
\]

\[
- \frac{i}{\hbar} \mu_{01}^2 e^{i \omega t} \int_0^\infty dt_1 E'(t - t_1) e^{-t_1/T_2} e^{2i \omega t}.
\]

To simplify the tedious convolution notation, a Feynman diagram is adopted to trace the coherence under the interaction between the electric field and the density matrix at different times graphically.

Below is an example of Feynman diagrams (Figure 2.1), displaying the four components in Equation (44). The vertical double line represents the ket (left) and bra (right) of the density matrix. From bottom to top is the time evolution, as shown by the arrow on the left side. The arrow pointing in or out from the density matrix represents the interaction with the dipole operator. An operator acting on ket corresponds to an arrow on the left side, and an operator acting on bra
corresponds to an arrow on the right side. The direction of the arrow is determined by the electric field. \( E(t) = E'(t)e^{-i\omega t} \) is represented by a right-pointing arrow. Its complex conjugate \( E'(t) = E'(t)e^{+i\omega t} \) is represented by a left-pointing arrow. The system propagates under its internal Hamiltonian in time intervals between laser pulses, experiencing processes including dephasing.

Feynman diagrams helps to identify which pathways need to be taken into consideration. In Figure 2.1, the first arrow in the pathways corresponding to \( R^{(1)}_2 \) and \( R^{(1)}_4 \) is pointing away from the density matrix, which represents emission of light and de-excitation of state. It means that the pulse tries to de-excite the ground state, which is rarely possible and in agreement with the rotating wave approximation results.

Feynman diagrams of four components in Equation (44).

2.1.7. Pathways in third-order spectroscopy

Similar to linear interaction, by instituting Equation (42) into third-order polarization, \( 2 \times 2^3 = 16 \) components are obtained.

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

\[
+ \langle \hat{\mu}(t_1 + t_2), [\hat{\mu}(t_1), [\hat{\mu}(0), \rho(-\infty)]] \rangle
\]
Denote $\hat{\mu}(0), \hat{\mu}(t_1), \hat{\mu}(t_1 + t_2), \hat{\mu}(t_1 + t_2 + t_3)$ as $\hat{\mu}_0, \hat{\mu}_1, \hat{\mu}_2,$ and $\hat{\mu}_3.$ Discard half of the 16 components according to rotating wave approximation; the remaining 8 pathways are described as:

$$R_1(t_1, t_2, t_3) = \left(\frac{i}{\hbar}\right)^3(\hat{\mu}_3\hat{\mu}_1\rho(-\infty)\hat{\mu}_0\hat{\mu}_2)$$ (47)

$$R_2(t_1, t_2, t_3) = \left(\frac{i}{\hbar}\right)^3(\hat{\mu}_3\hat{\mu}_2 \rho(-\infty)\hat{\mu}_0\hat{\mu}_1)$$ (48)

$$R_4(t_1, t_2, t_3) = \left(\frac{i}{\hbar}\right)^3(\hat{\mu}_3\hat{\mu}_0 \rho(-\infty)\hat{\mu}_1\hat{\mu}_2)$$ (49)

$$R_5(t_1, t_2, t_3) = \left(\frac{i}{\hbar}\right)^3(\hat{\mu}_3\hat{\mu}_2\hat{\mu}_1\hat{\mu}_0 \rho(-\infty))$$ (50)

$$R_1^*(t_1, t_2, t_3) = \left(\frac{i}{\hbar}\right)^3(\hat{\mu}_2\hat{\mu}_0\rho(-\infty)\hat{\mu}_1\hat{\mu}_3)$$ (51)

$$R_2^*(t_1, t_2, t_3) = \left(\frac{i}{\hbar}\right)^3(\hat{\mu}_1\hat{\mu}_0\rho(-\infty)\hat{\mu}_2\hat{\mu}_3)$$ (52)

$$R_4^*(t_1, t_2, t_3) = \left(\frac{i}{\hbar}\right)^3(\hat{\mu}_2\hat{\mu}_1\rho(-\infty)\hat{\mu}_0\hat{\mu}_3)$$ (53)

$$R_5^*(t_1, t_2, t_3) = \left(\frac{i}{\hbar}\right)^3(\rho(-\infty)\hat{\mu}_0\hat{\mu}_1\hat{\mu}_2\hat{\mu}_3)$$ (54)

$R_1^*, R_2^*, R_4^*, \text{ and } R_5^*$ are the complex conjugates of $R_1, R_2, R_4, \text{ and } R_5$ respectively. The pathways of $R_1, R_2, R_4, \text{ and } R_5$ are shown by Feynman diagrams in Figure 2.2. $R_3, \text{ and } R_6$ are omitted here, since they involved three-level system. These Feynman diagrams are shown in Figure 2.3.
Information of rephasing and non-rephasing is obtained from the Feynman diagrams. In the pathways $R_1$ and $R_2$, the two coherent states are $|0\rangle\langle1|$ and $|1\rangle\langle0|$, which are opposite. $|0\rangle\langle1|$ coherence is generated by $e^{i\omega t_1}$ oscillation of the density matrix off-diagonal element, while $|1\rangle\langle0|$ coherence is generated by $e^{-i\omega t_3}$ oscillation. Therefore, the dephasing in the time interval $t_1$ is compensated by the dephasing in the reversed direction in the time interval $t_3$. At the time $t_3 = t_1$, the initial phase condition is totally restored, so the $R_1$ and $R_2$ are named as rephasing pathways. In $R_4$ and $R_5$, the first and second coherent states are identical, which leads to a continuous increasing in dephasing. $R_4$ and $R_5$ are non-rephasing pathways.

The emitted signal generated by different pathways has its specific direction, so that the collection of signals generated by certain specific pathways without huge background of other beams is accessible. The direction of emitted light fulfills the phasing-matching condition, which will be discussed in Section 2.3.
2.2. Vibrational lineshape and spectra signatures

In the last section, we discussed the interaction between the molecular ensemble and the external electric field, going through the macroscopic polarization changes induced by laser pulse, and the emitted field generated by the oscillating polarization of the molecules. In this chapter, we are going into the spectra. Lineshape of linear and third-order nonlinear spectroscopy will be derived based on the emitted signal developed previously. Models will be built to interpret the relationship between macroscopic spectral signatures we observe, \textit{i.e.}, diagonal peak and crosspeak, and microscopic properties we want to investigate, \textit{i.e.}, dynamics and structure in the solution.

Figure 2.3. Feynman diagram of three-level system.
2.2.1. Linear spectroscopy lineshape

In typical linear infrared spectroscopy, the detector measures the intensity of the vector summation of both the incident electric field and signal. By taking the Fourier transform, the signal gathered by the detector is described as:

\[
S(\omega) \propto \left| \int_{0}^{+\infty} \left( E(t) + E_{sig}^{(1)}(t) \right) e^{i\omega t} dt \right|^2
\]

\[
\propto I_0(\omega) + 2\text{Re} \left\{ \int_{0}^{+\infty} E(t) e^{i\omega t} dt \cdot \int_{0}^{+\infty} E_{sig}^{(1)}(t) e^{i\omega t} dt \right\} + I_{sig}^{(1)}(\omega)
\]

\[
\approx I_0(\omega) + 2\text{Re} \left\{ E(\omega) \cdot E_{sig}^{(1)}(\omega) \right\}.
\]  \hspace{1cm} (55)

The intensity of the pure signal is much smaller than the intensity of incident light, so \(I_{sig}^{(1)}(\omega)\) is neglected. The signal is detected and amplified by the interference between incident light \(E\) and signal itself \(E_{sig}^{(1)}\), which is called as *heterodyned detection.*

The absorption in spectroscopy is defined as the additive inverse of the logarithm of the signal to incident ratio. Using the Taylor expansion of \(\ln(x)\), the absorption can be described as:

\[
A(\omega) = -\log \left( \frac{S(\omega)}{I_0(\omega)} \right) \approx 2\text{Re} \left\{ E(\omega) \cdot E_{sig}^{(1)}(\omega) \right\}.
\]  \hspace{1cm} (56)

Assume the electric field of incident pulse is a \(\delta\) function, and the dipole moment is a constant along time-evolution, substitute Equation (55), (39), and (45), the lineshape of absorption is described as a Lorentzian line:
\[ A(\omega) \propto \mu_{01}^2 \frac{1}{T_2^2} \left( \frac{\omega - \omega_0}{\omega - \omega_0} + \frac{1}{T_2^2} \right) \]  \hspace{1cm} (57)

2.2.2. Homogeneous and inhomogeneous dephasing

In the previous sections, the dephasing is treated simply with a homogeneous dephasing factor \( e^{-t/T_2} \), by assuming the frequency \( \omega_{01} \) of an oscillator does not change along time propagation. In this simplified case, the dephasing is caused by the increasing destructive interference among the emitted light from different molecules, which is called homogeneous dephasing. Now consider the time evolution of the molecular internal Hamiltonian influenced by the time evolution of the molecular environment, which leads to the inhomogeneous dephasing. Kubo’s theory is applied to describe the dephasing in the solution, where the molecular oscillator is treated quantum mechanically and the solution environment is treated classically.[4]

The time-dependent transition frequency is described as:

\[ \omega_{01}(t) = \omega_{01} + \delta \omega_{01}(t), \]  \hspace{1cm} (58)

where \( \omega_{01} \) is the average of \( \omega_{01}(t) \), and \( \delta \omega_{01}(t) \) is the fluctuation deviation from mean value at time \( t \). It fulfills the equation:

\[ \langle \delta \omega_{01}(t) \rangle = 0. \]  \hspace{1cm} (59)

The coherent element in the density matrix \( e^{\pm i\omega_0 t} e^{-t/T_2} \) now can be described as:

\[ e^{\pm i\omega_0 t} \langle \exp(-i \int_0^t d\tau \delta \omega_{01}(\tau)) \rangle. \]  \hspace{1cm} (60)
The time integral represents the time-dependent frequency fluctuation of a single molecule, and the \( \langle \ldots \rangle \) represents ensemble average of molecules. Plug Equation (60) into Equation (38), and assume the dipole moment is a constant when the environment fluctuates:

\[
R^{(1)}(t_1) = i \mu_{01}^2 e^{\pm i \omega_0 t} \langle \exp(-i \int_0^{t_1} d\tau \delta \omega_{01}(\tau)) \rangle
\]  

(61)

Denoting \( \langle \exp(-i \int_0^{t_1} d\tau \delta \omega_{01}(\tau)) \rangle \) as \( \exp(-g(t)) \), the dephasing term can be rewritten in the formulation of Taylor expansion:

\[
\langle \exp(-i \int_0^{t_1} d\tau \delta \omega_{01}(\tau)) \rangle = 1 - i \int_0^{t_1} d\tau \langle \delta \omega_{01}(\tau) \rangle \\
- \frac{1}{2} \int_0^{t_1} \int_0^{t_1} d\tau' d\tau'' \langle \delta \omega_{01}(\tau') \delta \omega_{01}(\tau'') \rangle + \cdots
\]

\[
\equiv \exp(-g(t)) = 1 - g(t) + \frac{1}{2} g^2(t) + \cdots
\]  

(62)

Expand \( g(t) \) in powers of \( \delta \omega_{01} \):

\[
g(t) = g_1(t) + g_2(t) + \cdots
\]  

(63)

where \( g_n(t) \) is on the order of \( O(\delta \omega_{01}^n) \). Substituting Equation (63) into (62), \( g_1(t) \) is found to be 0. Therefore, \( g(t) \) can be written as \( g_2(t) \) on the order of \( O(\delta \omega_{01}^2) \):

\[
g(t) = g_2(t) = \frac{1}{2} \int_0^{t_1} \int_0^{t_1} d\tau' d\tau'' \langle \delta \omega_{01}(\tau') \delta \omega_{01}(\tau'') \rangle,
\]  

(64)

which can be rewritten as:
\[ g(t) = \frac{1}{2} \int_0^t \int_0^{\tau'} \, d\tau' \, d\tau'' \langle \delta \omega_0(\tau'') \delta \omega_0(0) \rangle. \quad (65) \]

\( g(t) \) is called as the lineshape function, and \( \langle \delta \omega_0(\tau'') \delta \omega_0(0) \rangle \) is the frequency-frequency correlation function (FFCF). Substituting Equation (65) into Equation (61), the emitted signal of linear spectroscopy on frequency domain after Fourier transform is described as:

\[
S(\omega) \propto \text{Re} \left\{ \int_0^{+\infty} e^{i(\omega-\omega_0)t} e^{-g(t)} dt \right\}, \quad (66)
\]

where the information of the FFCF exists but hidden in the convolution.

### 2.2.3. Dynamics in FFCF and spectral diffusion

According to Kubo’s theory, assume the frequency fluctuation is a Markov process, FFCF can be described as the product of the square of the fluctuation amplitude \( \Delta^2 \) and an exponential decay with a correlation decay time \( \tau \):

\[
\langle \delta \omega(t) \delta \omega(0) \rangle = \Delta^2 e^{-\frac{t}{\tau}} \quad (67)
\]

Kubo lineshape function is obtained after two integrals:

\[
g(t) = \frac{1}{2} \int_0^t \int_0^{\tau'} \, d\tau' \, d\tau'' \langle \delta \omega_0(\tau'') \delta \omega_0(0) \rangle = \Delta^2 \tau^2 \left( e^{-\frac{t}{\tau}} + \frac{t}{\tau} - 1 \right) \quad (68)
\]

When \( t \gg \tau \), the frequency fluctuations are small or fast, and the dephasing dynamics is fast. The Kubo function is in the **homogeneous limit**, which can be written as

\[
g(t) = -\Delta^2 \tau t. \quad (69)
\]

Define the pure homogeneous dephasing time as:
\[ T_2^* = \frac{1}{\Delta^2 \tau}, \]  

(70)

Equation (69) can be rewritten as:

\[ g(t) = e^{-\frac{t}{T_2^*}}. \]  

(71)

Substituting Equation (71) to Equation (66), the frequency domain linear spectra is:

\[ S(\omega) \propto \frac{1}{(\omega - \omega_{01})^2 - \frac{1}{T_2^*^2}}, \]  

(72)

which is a Lorentzian function with a full width half maximum of \(1/T_2^*\). This reduces to Equation (57), where we treated the dephasing simply with a homogeneous dephasing factor. *Motionally narrowed* Lorentzian lineshape will be observed, since \(1/T_2^*\) is smaller than the frequency fluctuation distribution \(\Delta\).

When \(\tau \gg t\), which is corresponding to the slow frequency fluctuation of molecules, it is the *inhomogeneous limit*. Therefore, the FFCF is a constant:

\[ \langle \delta \omega(t) \delta \omega(0) \rangle = \Delta^2 \]  

(73)

The Kubo lineshape function can be rewritten as:

\[ g(t) = \frac{\Delta^2 \tau^2}{2}, \]  

(74)

So the frequency-domain linear spectra is obtained as:

\[ S(\omega) \propto \text{Re} \left\{ \int_0^{+\infty} e^{i(\omega-\omega_{01})t} e^{-g(t)} dt \right\} \propto e^{-\frac{(\omega-\omega_{01})^2}{2\Delta^2}}, \]  

(75)

which is a Guassian function with a full width half maximum of \(\Delta\).
For the case between homogeneous limit and inhomogeneous limit, the spectra is a convolution of a Lorentzian function and a Gaussian function, which is a Voigt profile. In the case that the frequency fluctuation has more than one physical process, the FFCF will have more than one exponential decay components, with each component has a correlation decay time of each physical process.

In the 2DIR spectroscopy, frequency fluctuation results in the spectral diffusion phenomenon. It is a time-propagation diagonal peak shape change, from a tilted shape elongated along the diagonal line to a rounder and more upright shape, which can be simply understood as the probe frequency gets deviated from the pump frequency as waiting time increases because of the frequency fluctuation. FFCF can be obtained directly from the 2DIR spectroscopy using the central line slope or the nodal line slope.[5, 6]

2.2.4. Anharmonicity

Consider a third-order nonlinear response process. After first two laser pulses, the system is located in population states of \(|1\rangle\langle1|\) or \(|0\rangle\langle0|\). After this point, there are three possible processes.

For those at ground state \(|0\rangle\langle0|\), the third pulse generates a coherence state between \(|0\rangle\langle1|\) and \(|1\rangle\langle0|\), and goes back to \(|0\rangle\langle0|\) population state with a decreasing of absorption at frequency \(\omega_{01}\), which is called as the ground-state bleach.

For those at excited state \(|1\rangle\langle1|\), the third pulse can leads to either a coherence between ground state \(|0\rangle\langle0|\) and first excited state \(|1\rangle\langle1|\), or a coherence between first excited state \(|1\rangle\langle1|\) and second excited state \(|2\rangle\langle2|\). The former causes a decreasing in absorption at frequency \(\omega_{01}\), and the
latter causes an increasing in the absorption at frequency \( \omega_{12} \), which are named as the *stimulated emission* and *excited absorption* respectively.

The three processes result in two points on the 2DIR spectra. At same pump frequency \( \omega_{01} \), the ground-state bleach and stimulated emission locates at \((\omega_{01}, \omega_{01})\), while the excited absorption locates at \((\omega_{01}, \omega_{12})\). It results in the phenomenon that the diagonal peaks in 2DIR appear in pairs. The frequency difference between these two peaks rises from the anharmonicity of the oscillator energy potential surface. In a conventional potential well of oscillator, including the harmonic oscillator, \( \omega_{01} \) is larger than \( \omega_{12} \), which means the excited absorption shifts to lower frequency compared with ground-state bleach and stimulated emission on the diagonal line. When the anharmonicity is reversed, which occurs in the very steep potential well as observed in delocalized excess protons in water cluster, the excited absorption shifts to higher frequency compared with ground-state bleach and stimulated emission. When the anharmonicity is 0, the two peaks overlap.

### 2.2.5. Crosspeak

In 2DIR spectra, there also sometimes exists crosspeak besides the diagonal peaks. Crosspeaks appear off the diagonal line, with its pump and probe pulses having different central frequencies.

Static crosspeak appearing at very short waiting time \( t_2 \) on the order of femtoseconds can be related to the coupling among different vibrational modes. When the local modes are strongly coupled, delocalized states are formed, which is called as the *vibrational exciton*. The Hamiltonian of coupling between two vibrational modes focused on the transition between the ground state and the first-excited state is described as:
\[ \hat{H} = \begin{pmatrix} \hbar \omega_1 & \beta_{12} \\ \beta_{21} & \hbar \omega_2 \end{pmatrix}, \]  

where \( \omega_1 \) and \( \omega_2 \) are corresponding to the Hamiltonian of isolated vibrational modes respectively, and \( \beta_{12} \) and \( \beta_{21} \) is the coupling constant. Assume \( \beta_{12} = \beta_{21} \).

In weak coupling limit, where \( \beta_{12} \ll |\hbar \omega_1 - \hbar \omega_2| \), the Eigen value of energy is solved as:[7]

\[ E_{1,2}^{\text{exciton}} = \hbar \omega_{1,2} \pm \frac{2 \beta_{12}^2}{\hbar \omega_2 - \hbar \omega_1}. \]  

In strong coupling limit, where \( \beta_{12} \gg |\hbar \omega_1 - \hbar \omega_2| \), the Eigen value of energy is:

\[ E_{1,2}^{\text{exciton}} = \frac{\hbar \omega_1 + \hbar \omega_2}{2} \mp \beta_{12}. \]  

The anharmonicity of the crosspeaks varies from that of corresponding diagonal peaks because of the delocalization. In the case of strong coupling, anharmonicity of crosspeaks is much larger than diagonal peaks, and in the case of weak coupling, anharmonicity of crosspeaks is smaller than diagonal peaks.

Static crosspeak can also come from an intramolecular coupling called \textit{Fermi resonance}. Fermi resonance appears when a transition accidentally has a similar frequency as an overtone or a combination mode. Moreover, this resonance is unpredictable before doing experiment, and is an obstacle when analyzing 2DIR data.

The time evolution of crosspeak could be related to different dynamic processes. One possible reason is the \textit{population transfer}, which happens between the coupled vibrational modes that have similar vibrational energies. This time evolution could also yield from the so-called chemical exchange. In this case, the oscillator exists in two distinguished types of environment in solution, which means they do not result in small deviations around the same central frequency, but two distinguished peaks with two different central frequencies instead. In the process of
chemical exchange, the molecule is pumped in one environment, and probed when it moves to the other environment.

2.3. Implementation of 2DIR spectroscopy

2.3.1. Generation of ultrafast femtosecond laser pulse

The source of the ultrafast laser pulse for 2DIR set-up is generated by Mai Tai SP mode-locked Ti:Sapphire laser with a Spitfire Ace regenerative Ti:sapphire amplifier. The Mai Tai SP laser consists of a CW diode-pumped, intracavity, solid-state laser chamber and a Ti:Sapphire laser chamber. In the first chamber, the output of diode laser is used to pump Nd$^{3+}$ ion in Nd:YVO$_4$ medium, and the frequency-doubled output (532 nm) of Nd:YVO$_4$ laser using second harmonic generation is used to pump the Ti:Sapphire laser in the second chamber. In the second chamber, the material responsible for lasing is the Ti:Sapphire rod in the cavity between two mirrors. An acousto-optic modulator is applied to achieve the mode-locked operation. The output of Ti:Sapphire laser with a wavelength of 800 nm then undergoes a tuning process and enters the Spitfire amplifier. The amplifier consists of a stretcher, which lowers the pulse power to avoid threshold damage, a cavity, which amplifies the pulse, and a compressor, which compresses the pulse period. The Mai Tai laser along with Spitfire generates stable pulses centered at 800 nm with a repetition rate of 5 kHz and an average power of 1 W.

A chiller is used to water-cool and control the temperature of the crystals in CW pump laser and Ti:Sapphire laser to ensure a stable laser performance. The laser head is sealed to prevent dust and air moisture.
The vibrational frequency of investigated modes is in the mid-infrared region. As a result, an optical parametric amplifier (OPA) is applied to generate stable ultrafast pulses in the infrared region with the 800 nm pulse from the amplifier. The simplified set-up of OPA-800C system is shown in Figure 2.4. The input light is split into two beams after the first beam splitter. About 96% of the energy is transmitted and used for the OPA pump. The 4% reflected light is used to generate a white light as a seed pulse for wavelength extension by focusing on a 2 mm thick sapphire plate. The pump beam passes the second beam splitter and is split again into two beams. Pump 1 and the re-collimated delayed white light focus on a BBO crystal (β-BaB$_2$O$_4$, type II) to pre-amplify the frequency component. Pump 2 then hits the pre-amplified continuum reflected back by the white-light reflector on the same BBO crystal at another spot to generate a signal and an idler. The signal and idler cover the wavelength from 1.1 µm to 1.6 µm, and from 1.6 µm to 3.0 µm respectively.
Finally, the signal and idler generate an ultrafast infrared laser pulse with the wavelength from 3 μm to 10 μm on the AgGaS$_2$ crystal (type II) by difference frequency generation.

### 2.3.2. 2DIR experimental set-up

Ultrafast laser pulses from OPA is split into four beams after two beam splitters. Three of them are used as external electric fields applied on the investigated sample, which is prepared between two windows that do not have absorption in the frequency region we look into (usually CaF$_2$). The path length of the lights is determined by the thickness of the spacer put between the two windows.

The emitted light is detected in the direction determined by the *phase-matching condition*. Light propagates in the space is not only a function of time t and phase $\phi$, but also related to the propagation vector $k$, and its position. Therefore, an electric field can be described as:

$$ E = E' e^{-i(\vec{k} \cdot \vec{r} - \omega t + \phi)}. \quad (79) $$

Denote the propagation vector of three pulses as $\vec{k}_1$, $\vec{k}_2$, and $\vec{k}_3$ at the time sequence. All of them are at different directions. The third-order macroscopic polarizations of rephasing pathway $R_1$ and non-rephasing pathway $R_4$ are described as:

$$ P_1^{(3)} \propto e^{i(-\vec{k}_1 + \vec{k}_2 + \vec{k}_3) \cdot \vec{r}} e^{i(-\phi_1 + \phi_2 + \phi_3)} \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 E_3''(t - t_3) \cdot E_2''(t - t_3 - t_2) \cdot E_1''(t - t_3 - t_2 - t_1) R_1(t_1, t_2, t_3), \quad (80) $$

and:
\[ P_4^{(3)} \propto e^{i(k_1 - k_2 + k_3) \cdot \vec{r}} e^{i(\phi_1 - \phi_2 + \phi_3)} \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 E_3'''(t - t_3) \]
\[ \cdot E_2^{*'''}(t - t_3 - t_2) \cdot E_1''(t - t_3 - t_2 - t_1) R_4(t_1, t_2, t_3). \]

So the propagation vector of \( P_1^{(3)} \) is \(-\vec{k}_1 + \vec{k}_2 + \vec{k}_3\), and the propagation vector of \( P_4^{(3)} \) is \( \vec{k}_1 - \vec{k}_2 + \vec{k}_3 \). The rephasing signals then can be separated from non-rephasing ones, but not among themselves. To collect both rephasing and non-rephasing signals, although it is possible to put two detectors in different directions, it is more convenient to exchange the pulse sequence of \( \vec{k}_1 \) and \( \vec{k}_2 \). \( P_1^{(3)} \) is positive only if \( t_1 \geq 0, t_2 \geq 0, \) and \( t_3 \geq 0 \). Therefore, if \( \vec{k}_2 \) arrives the sample before \( \vec{k}_1 \) by scanning the time stage of pulses, the other type of signal can be collected in the same phasing matching direction. This configuration of three incident pulses is called as boxcar configuration.

The emitted light is heterodyned detected by the fourth pulse, \( i.e. \), local oscillator, from the beam splitter to amplify the signal, which is called heterodyne detection. The intensity of the interference is detected by a nitrogen-cooled 64-element MCT array detector through a monochromator.
2.4. **Computational methods**

Molecular dynamics (MD) simulation is a useful tool to help investigate the dynamics and structure in the many-body systems by simulating it numerically on the atom scale. Experimental spectroscopy measures macroscopic properties directly and investigates microscopic structure and dynamics by making assumptions and building models that relate to the microscopic properties with the macroscopic ones. MD simulation looks into the microscopic processes directly, and becomes a good tool besides the experimental methods.

The input for an MD simulation is the initial position, velocity, and the mass of all the atoms in the system, then the movement of all atoms is calculated for each time step, which is
normally on the order of femtosecond when investigating the dynamics in the condensed phase. In
each step, forces on each atom are obtained first, then the new positions and velocities can be
calculated. In this section, both the classical MD simulation and *ab initio* MD simulation will be
discussed.

2.4.1. Classical MD simulation

Classical MD simulation treats every single atom (or united atoms) under Newton’s Law. The implement is to calculate forces from a parameterized force field, which is firstly building a model to describe interactions and then either fitting the variables from experimental data, or from high-level calculations.

The overall energy potential is typically divided into four components:

\[ V(\vec{r}) = V_{\text{bonded}} + V_{\text{non-bonded}} + V_{\text{restraints}} + V_{\text{field}}. \]  

The bonded interaction potential \( V_{\text{bonded}} \) is represented by terms dependent on bond length, bond angles, and torsional angles respectively.

The 2-body pair potential is described as a harmonic vibrational potential between the two covalently bonded atoms \( i \) and \( j \):

\[ V_{\text{bond}}(r_{ij}) = \frac{1}{2} k_{ij}^b (r_{ij} - r_{ij}^0)^2, \]  

where \( k_{ij}^b \) is the spring constant, \( r_{ij} \) is the distance between two atoms, and \( r_{ij}^0 \) is the equilibrium distance.

The 3-body angular potential is also described by a harmonic vibrational potential, but among three covalently bonded atoms \( i, j, \) and \( k \):
\[ V_{\text{angle}}(\theta_{ijk}) = \frac{1}{2} k_{ijk}^\theta \left( \theta_{ijk} - \theta_{ijk}^0 \right)^2, \quad (84) \]

where \( k_{ijk}^\theta \) is the angle force constant, \( \theta_{ijk} \) is the angle in radians between \( \vec{r}_{ij} \) and \( \vec{r}_{kj} \), and \( \theta_{ijk}^0 \) is the equilibrium angle.

The 4-body dihedral angle (torsion) potential is divided into two categories: proper dihedral angle and improper dihedral angle. The former is formed by four consecutive atoms, while the latter is formed by three atoms centered around a fourth atom. The quartet potentials are described by:

\[ V_{\text{proper torsion}}(\phi_{ijkl}) = k_{ijkl}^C \left( 1 + \cos(n\phi_{ijkl} - \phi_0) \right), \quad (85) \]

\[ V_{\text{improper torsion}}(\phi_{ijkl}) = \frac{1}{2} k_{ijkl}^H \left( \phi_{ijkl} - \phi_{ijkl}^0 \right)^2. \quad (86) \]

\( k_{ijkl}^C \) is the force constant of the cosine type, and \( k_{ijkl}^H \) is the force constant of the improper torsion. \( \phi_{ijkl} \) is the angle between the plane going through the atoms \( i, j, k \), and the plane going through \( j, k, l \). \( \phi_0 \) and \( \phi_{ijkl}^0 \) are the equilibrium torsion, where the energy potential has its minimum value. \( n \) is the multiplicity, which is the number of minima in the interaction potential as the dihedral angle rotates 360 degrees.

Non-bonded n-body interactions \( V_{\text{non-bonded}} \) are treated by an effective pair potential for simplicity and computational efficiency.

The most famous potential model for non-bonded interactions is the Lennard Jones potential, which describes the Van der Waals potential as:
\[ V_{LJ} = \sum_{i<j} 4\varepsilon \left[ \left( \frac{\sigma}{R_{LJ}} \right)^{12} - \left( \frac{\sigma}{R_{LJ}} \right)^{6} \right] \] (87)

where \( \varepsilon \) is the depth of the potential well, \( \sigma \) is the finite distance where the potential is zero, \( r \) is the distance between the atoms.

Another common model for non-bonded interaction potential is the Coulomb potential, which describes the electrostatic interaction between two atoms:

\[ V_{\text{Coul}} = \sum_{i<j} \frac{q_i q_j}{4\pi \varepsilon_0 \varepsilon_R r_{ij}} , \] (88)

where \( q_i \) and \( q_j \) are charges of the two atoms respectively. \( \varepsilon_0 \) is the permittivity of vacuum, \( \varepsilon_R \) is the dielectric constant of the media, and \( r_{ij} \) is the distance between two atoms.

Restraint potentials \( V_{\text{restraints}} \) are used to restraint the motion of systems to avoid disastrous deviation, to fit for specific experimental data, or to accomplish sampling. Restraint potentials are not real potential and have numerous types, such as position restraint, angle restraint, torsion restraint, distance restraint, and orientation restraint, to implement different needs in computational simulation.

Fields \( V_{\text{field}} \) are usually applied to describe two things: external potentials exerted on the system, which could be external electromagnetic field or flow; and continuum solvation, which approximates the solvent as the implicit continuous medium with several properties such as dielectric constant instead of the explicit solvent molecules.

Verlet algorithm is often applied in order to obtain the time propagation of velocity and position in each step.[8] The iteration is:
\[ r(t + \delta t) = 2r(t) - r(t - \delta t) + f(t)/m \cdot \delta t^2, \]  \hspace{1cm} (89)

Periodic boundary conditions are applied to minimize the edge effect and maintain the macroscopic behavior of the system. It is implemented by filling the universe with infinitive periodic replicas of fundamental boxes, which means a particle exiting one side of the box will enter the box from the opposite side. The cubic box is the most common box shape, while other shapes such as rhombic dodecahedron, truncated octahedron, are also available. Minimum image convention is used to ensure a correct short-range interaction picture, and long-range interactions and fluctuations with wavelength larger than box size might be not well described.

The classical MD simulation is convenient because it’s much faster compared with \textit{ab initio} simulation. This classical MD treatment can simulate large systems for very slow dynamics without consuming too much time. The disadvantages include, it is not as exact as the quantum treatment which solves Schrodinger equations. Especially when there is charge transfer, proton hopping, and other quantum effects, the classical MD cannot predict the system evolution correctly. Another problem is that one force field is fitted for one specific kind of system, so if the system is not parametrized before, you have to build a new force field yourself.

\textbf{2.4.2. AIMD simulation}

AIMD simulation invented by Car and Parrinello is a lot more exact compared with classical MD simulation since it does not have any empirical potential parameters. All the potentials are solved by time-dependent Schrodinger function. [9]

Solving the time-dependent Schrodinger function of the many-body system is prohibitively expensive. It became reachable after the Density Functional Theory (DFT) was proposed.[10]
Although other methods such as MP2 are developed and applied, DFT is still the most popular one.\[11\]

DFT method is based on the Born–Oppenheimer (BO) approximation, wherein the motions of nuclei and motions of electrons can be treated separately. Instead of using a big amount of wavefunctions to describe each electron respectively, DFT theory describes the electron structure of the whole system using only one potential, and all the interaction terms are hidden, which reduces the quantity of interest from 3n dimensions to 3 dimensions. System of n electrons can be studied as a set of n one-electron Schrödinger-like equations, which are called Kohn–Sham equations: \[12\]

\[
-\frac{1}{2}\nabla^2 + V_{\text{eff}}(r) \phi_i(r) = \epsilon_i \phi_i(r). \tag{90}
\]

The first term is kinetic energy functional, and the second term effective potential is:

\[
V_{\text{eff}} = V_{\text{ext}} + \int \frac{n(r')}{|r - r'|} \, dr' + \frac{\delta E_{\text{xc}}[n(r)]}{\delta n(r)}, \tag{91}
\]

where $V_{\text{ext}}$ is the external potential functional, $\int \frac{n(r')}{|r - r'|} \, dr'$ is called the Hartree term, which describes the direct Coulomb interaction between electron, and the last term $\int \frac{n(r')}{|r - r'|} \, dr'$ represents exchange-correlation energy.

Currently, it is proved that to obtain the exact exchange-correlation functional is prohibitive.\[13\] Therefore, approximations need to be made, and the exchange-correlation functionless of different level of approximation are developed. The accuracy increases as more complicated models are developed: Local Density Approximation (LDA), Generalized Gradient Approximation (GGA), meta-GGA, Hybrid Functional (HF) and etc.\[14\]
2.5. Conclusion

In this chapter, we discussed the light-matter interaction in the infrared spectroscopy, derived the molecular response function for linear and nonlinear processes, and went through both the rephasing and non-rephasing pathways. Then we derived the frequency domain spectra that could be gathered from the detector while building a relationship between the 2DIR observables and the physical processes. After that, setups for the ultrafast infrared pulse generation, and for the 2DIR experiment are discussed. Finally, computational methods to simulate the molecular dynamics are introduced.

2.6. References


CHAPTER 3
ACETATE ION AND ITS INTERESTING SOLVATION SHELL
STRUCTURE AND DYNAMICS

3.1. Introduction

Ions are crucial species in medicine, biology, chemistry, and engineering due to their participation in important processes like nerve signaling,[1] ion transport through membranes,[2] chemical synthesis,[3] and electrochemical energy conversion.[3] Thus, in general, a basic characterization of the microscopic and macroscopic solvation phenomena of ions is extremely important from both a scientific and an engineering point of view. Ions are classified into two categories. The first category involves simple inorganic ions like Na⁺, Zn²⁺, and Cl⁻, which are formed by reducing or oxidizing the atomic elements. The second category comprises ionized polyatomic molecular species; i.e., molecular ions, such as acetate, nitrate, and phosphate ions. Although simple inorganic and molecular ions share similar interactions with water molecules, the small difference in the interaction potential leads to large differences in the structure and dynamics of their hydration shell.[3]

One of first studies on ion hydration dates back more than 100 years, when Hofmeister showed the salting-out and salting-in effects that different ions exert on proteins, which is now known as the famous Hofmeister series.[4] The discovery of this series led to the definition of kosmotropes and chaotropes; i.e., water structure makers and breakers.[5] Interestingly, the

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definition of water structure makers and breakers did not arise from a microscopic analysis of the water structure, but from the macroscopic effects of the ions, such as protein precipitation, bacterial growth, etc.[6] However, it was until the last two decades, that the microscopic structure and dynamics of the ion hydration shell started to be directly investigated via advanced ultrafast laser spectroscopies and, in particular, third order non-linear infrared spectroscopy.[3] As a result, the hydration dynamics and structure of molecular ions, such as thiocyanate,[7-9] azide,[10-12] guanidinium,[13] oxalate,[14-16] phosphate,[17] nitrate,[18] hydroxide,[19, 20] borohydride,[21] etc. had been now studied. In addition, solvation structure of other ions like alkali halides have been indirectly investigated.[22-24] Notably, the hydration structure and dynamics of the acetate ion, an equally important molecular ion, has not been fully investigated yet.

Acetate (CH$_3$COO$^-$) is an ion with large applications in industry and important implications in life. In fact, the acetate ion is crucial for the synthesis of numerous derivatives like acetyl coenzyme A, citric acid, and oxaloacetate in cell organisms.[25] In addition, acetate ion is an analogue of a moiety commonly found in many important biomolecules, such as amino acids, lipids, and osmolytes, where the carboxylate group is covalently attached to a larger structure through a hydrophobic methylene group (-CH$_2$-).[25] Previous studies on the acetate ion solvation showed its interesting and unique properties.[4, 26-31] However, some of these studies reached contradictory conclusions. For example, the order of the activity coefficients for given concentration alkali in acetate (Li$^+$ < Na$^+$ < K$^+$ < Rb$^+$ < Cs$^+$) was found to be reversed in comparison with alkali chloride salts, and was explained by “localized hydrolysis.”[26] In contrast, it was postulated that acetate ions are structure-makers because the hydrophobic group (methyl, -CH$_3$) has a comparatively larger effect than its hydrophilic groups (carboxylate, -CO$_2^-$).[4]
Moreover, a dielectric relaxation spectroscopy (DRS) study showed that the acetate ion presents two slow components in the dielectric spectrum, which were assigned to the hydration dynamics of the carboxylate and methyl groups, respectively. However, the dynamical component corresponding to the methyl group was observed to be fragile and to decrease markedly with increasing concentration.[27] Finally, it was found experimentally that the acetate ion presents a lower diffusivity than that predicted by the Stoke-Einstein relation indicating a tight binding to its solvation shell.[30] The observation is in agreement with the acetate Jones-Dolle’s B-coefficient of \( B = 0.10 \pm .02 \text{ M}^{-1} \) derived from Ref. [32]. Furthermore, it has been previously demonstrated by Hamm and Laage groups that those ions that bind tightly to its solvation shell should slowdown the rearrangements of the hydrogen bond network.[33, 34]

Other studies indirectly probing the hydration particularity of acetate have shown experimentally that the acetate ion does not form contact ion pairs.[29] A molecular simulation study explained the lack of ion pair formation by thermodynamics, since the contact ion pair of acetate was found to be of entropic origin, while the solvent-shared ion pair was mainly enthalpically favorable.[28] Thus, it remains as an open question whether the water solvation shell around the acetate ion is strengthened or weakened by the acetate ion. Furthermore, the molecular mechanism behind the lack of contact ion pair formation by the acetate ion is still unknown. To this end, a detailed microscopic description of the hydration shell dynamics and structure of acetate ion in solution is needed.

In this study, dilute solutions of sodium acetate (0.1M) in pure D\(_2\)O (referred as water in the rest of the manuscript) and in 6M NaCl solution are studied via linear and non-linear infrared (IR) spectroscopies and \textit{ab initio} molecular dynamics simulation (AIMD). The selected non-linear
spectroscopy is two dimensional infrared spectroscopy (2DIR) because it can measure the dynamics of solvent motions from femtoseconds to picosecond timescales.[35] The IR studies are focused on the carboxylate asymmetric stretch mode of the acetate ion to investigate its hydration shell dynamics, because it has been previously established that this group is a sensitive probe to the local environment for other ions,[14, 16, 36, 37] zwitterions,[38] and peptides.[39, 40] The experimental findings are complemented with AIMD simulations and a frequency map to uncover and/or confirm the molecular processes giving rise to the observed vibrational dynamics of the acetate ion.

3.2. Experimental and theoretical methods

3.2.1. Sample preparation

Deuterium oxide (D$_2$O, >=99.75 % D) was obtained from Acros Organics. Sodium acetate (NaC$_2$H$_3$O$_2$, 99%), sodium azide (NaN$_3$, 99.8%), and sodium chloride (NaCl, 99.0%) were purchased from MCB reagents, Sigma Aldrich, and Fisher Chemical, respectively. All chemicals were used without further purification, except for the sodium acetate that was dried in the vacuum oven previous to its use. Sodium acetate and sodium azide were dissolved in D$_2$O and 6M NaCl D$_2$O solution, respectively, to obtain 0.1M solutions. The acetate and azide samples were held in between two CaF$_2$ windows separated by a spacer of 12 µm and 25 µm, respectively. All experiments were measured at room temperature (23 ºC).
3.2.2. Infrared spectroscopies

The Fourier transform IR (FTIR) spectra were collected with a Bruker Tensor 27 spectrometer with a resolution of 0.5 cm\(^{-1}\). Each reported FTIR spectrum is an average of 40 scans.

The setup used consists of the typical boxcar configuration photon echo setup with heterodyne detection.[35] In short, broadband IR pulses, with a temporal width of \(\sim 60\) fs, are generated by a Ti:Sapphire amplifier (Spectra Physics Spitfire Ace) with a 5 kHz repetition rate in combination with an optical parametric amplifier (Spectra Physics OPA-800C) and difference generation crystal. The non-linear response of the sample is produced by focusing and temporally and spatially overlapping three split replicas (wave vectors: \(k_1\), \(k_2\), and \(k_3\)) of the original IR pulse at the sample using the boxcar configuration. The photon echo signal produced by the sample is collected in the phase matching direction \((-k_1 + k_2 + k_3)\) and heterodyned with a fourth IR pulse (local oscillator) for detection. The detection occurs in a liquid nitrogen cooled 64 element MCT array detector (Infrared Systems Development) after the photon echo and local oscillator are dispersed in a Triax monochromator (100 grooves/mm). Two pulse sequences, rephasing (with a time order \(k_1 < k_2 < k_3\)) and non-rephasing (with a time order \(k_2 < k_1 < k_3\)) are measured to obtain the 2DIR spectra. The coherence time interval \(\tau\) was scanned from -3500 fs to 3500 fs with a step of 5 fs, and the waiting time \(T\) was scanned with a step of 150 fs from 0 ps to 2.1 ps. In all the cases, the local oscillator preceded the photon echo signal by \(\sim 1\) ps. The 2DIR spectra were obtained by a double Fourier Transformation on the photon echo signal from \((\tau, T_w, t)\) to \((\omega_\tau, \omega_w, \omega_t)\), while \(T_w\) is kept as a parameter. A detail explanation of this analysis can be found elsewhere.[41]
3.2.3. *Ab initio* molecular dynamics (AIMD) simulation

The system was selected to be model via AIMD simulations because of the reproducibility of the self-diffusion coefficient of water molecules in solutions with high salt concentration.[42] The simulation boxes for sodium acetate in water and sodium acetate in salt solutions were built by Packmol.[43] Due to high computational cost of the AIMD, the selected box size was 15Å×15Å×15Å. In this box, the 0.1M sodium acetate solution was represented by 113 water molecules and one sodium acetate molecule, while the 0.1M sodium acetate salt solution consisted of 121 water molecules, six Na\(^+\) ion, six Cl\(^-\) ion, and one sodium acetate molecule, or equivalent 3 M NaCl. Note that the 3 M NaCl solution was used because the simulation at 6 M NaCl produced phase separations. The concentration of acetate in simulation is larger than 0.1M due to the limitation of the box size for performing AIMD simulations. However, the box contains only one acetate ion, which inhibits acetate-acetate interactions, and it is sufficiently large to accommodate both ions without forming ion pairs all the time.

Classical molecular dynamics simulations (MD) were first performed to achieve equilibrated states which are later used as starting points for the AIMD simulations. Classic MD simulations with periodic boundary conditions were carried out by Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)[44] with the input files generated by moltemplate software[45] using the Optimized Potentials for Liquid Simulations (OPLSAA) force field.[46] The TIP3P water model was chosen for describing the water molecules in the solution.[47] The systems first underwent a 1 ns canonical simulation (in the NVT ensemble) followed by a 1 ns isothermal-isobaric simulation (in the NPT ensemble) to achieve equilibrium. Finally, the whole system underwent another 5 ns of canonical simulation as production run. In all cases, the
simulation temperature was 300 K and Nose-Hoover thermostat with a damping constant of 100 fs was used. In the NPT simulation, a Nose-Hoover barostat with a damping constant of 1 ps was used. The time step in all the simulations was 1 fs. About 15 snapshots from the final NVT simulation of each system were randomly chosen and used as starting configurations for the AIMD simulations.

The AIMD simulations were performed using the CP2K software package.[48] The simulations were carried out using the BLYP functional with TZV2P basis set and GTH pseudopotentials for the inter core electrons.[49] The functional as well as the basis set were selected because they have been shown to reproduce both the structural and dynamical properties of water.[50] All simulations were carried out in the NVT ensemble with periodic boundary conditions and a temperature of 300K. The temperature was maintained by using a Nose-Hoover thermostat with a 100 fs temperature damping constant. For sodium acetate in water, 13 trajectories of AIMD simulation were obtained, each having a temporal length of 6.5 ps with a step of 0.5 fs. The first 0.5 ps in each trajectory was discarded from the analysis to assure that the system had reached equilibrium. For sodium acetate in NaCl solution, only nine of the 15 original trajectories were used because the other six have contact ion pairs, but the vibrational signature of ion pairs is spectrally separated from that of the free ion (see below). In addition, the inclusion of ion pairs fail to produce a good estimate of the FFCF (not shown). Each trajectory for the acetate ion in NaCl solution has a temporal length of 7 ps with a time step of 0.5 fs. In this case, the first 1 ps of the trajectory was discarded to allow the system to reach equilibrium conditions.
3.2.4. Theoretical frequency-frequency correlation function

A density functional theory (DFT) map developed for the acetate ion was used to derive the frequency fluctuations of its carboxylate asymmetric stretch mode in pure water and in NaCl solution from the AIMD simulation.[40] The DFT map relates the solvent structural fluctuation with the vibrational frequency by empirically linking the vibrational mode frequency with electric fields exerted by the solvent molecules on the atoms involved in the vibrational mode. In this case, the vibrational mode is the asymmetric stretch of acetate and the electric fields are computed on the carbon and oxygen atoms of the carboxylate group.[40] The frequency of the mode is calculated based on the equation, \( \omega[E(r)] = \sum C_{ij}E_i(r_j) \), where \( \omega[E(r)] \) is the frequency of the transition between ground state and first excited state in the electric field \( E \), \( E_i \) is the electrostatic field or its gradient, \( C_{ij} \) is the empirically determined electrostatic parameters obtained from the DFT map, \( i \) is the directions of the field or the gradient (\( i = x, y, z, xx, yy, zz, xy \)), and \( j \) represents the atom at which the fields and the gradients are calculated.

The instantaneous frequencies of the carboxylate asymmetric stretch mode were calculated at each time step in the AIMD simulation trajectory using the DFT map. The electric fields and gradients generated by water molecules from the first solvation shell were computed from the coordinates of AIMD trajectories. Note that the charges of the water molecules were assumed to be those from the TIP3P water model because this model was used for creating the DFT map.[40, 47] The fluctuation of the instantaneous frequencies \( (\omega(t)) \) was computed as: \( \delta\omega(t) = \omega(t) - \langle \omega \rangle \), where \( \langle \omega \rangle \) is the average of the frequency of all the trajectories. The frequency-frequency correlation function (FFCF) was computed as the average of the individual correlation functions (i.e., \( \langle \delta\omega(0)\delta\omega(t) \rangle \)) derived for each trajectory.
3.3. Results

3.3.1. FTIR spectroscopy

The FTIR spectra of 0.1M sodium acetate in D$_2$O and in 6M NaCl solution are shown in Figure 3.1. The solvent subtracted spectra exhibits two peaks located at ~1420 cm$^{-1}$ and ~1560 cm$^{-1}$. The high frequency peak has been previously assigned to the antisymmetric stretching mode of the carboxylate group (AS$_{\text{COO}}$), and the partially overlapped peak at ~1420 cm$^{-1}$ to its symmetric stretching mode.[51] At low frequencies, there is another small peak at ~ 1350 cm$^{-1}$, which is likely from the symmetric CH$_3$ deformation.[52] The comparison between the spectra of sodium acetate in 6M NaCl solution and in D$_2$O shows that there is no obvious difference in bandwidth and central frequency for the modes observed in this region, aside from the difference in the low frequency part due to background subtraction errors caused by the presence of both the combination mode of D$_2$O at ~1555 cm$^{-1}$ and the bending mode at ~1210 cm$^{-1}$.[53] Furthermore, the bands of the AS$_{\text{COO}}$ observed for the acetate ion in D$_2$O and NaCl solutions have almost a perfect overlap (inset Figure 3.1). Finally, the IR spectrum of acetate in the carboxylate symmetric and asymmetric stretch region does not appear to be concentration dependent (Figure 3.2).
Figure 3.1. Solvent subtracted FTIR spectra of 0.1 M sodium acetate (top panel) and 0.1 M sodium azide (bottom panel) in the asymmetric stretch region of O=C=O and N=N=N. Black solid and red dashed lines correspond to D$_2$O and 6M NaCl solutions, respectively.

Figure 3.2. Concentration dependence of the carboxylate symmetric and asymmetric stretch of carboxylate in acetate.
3.3.2. Two dimensional infrared spectroscopy (2DIR)

The 2DIR spectra of sodium acetate in D$_2$O and in sodium chloride solution at the frequency range of the AS$_{\text{COO}}$ for different waiting times (T$_W$) is shown in Figure 3.3. In these 2D spectra, the horizontal ($\omega_t$) and vertical ($\omega_\tau$) axes represent the probe and pump frequencies, respectively. Each 2DIR spectrum shows a negative peak (blue right peak) and a positive peak (red left peak), which are related to the transitions of the AS$_{\text{COO}}$ from the vibrational ground state to the first excited state (ν=0 to ν=1), and from the first excited state to the second excited state (ν=1 to ν=2), respectively. The ~30 cm$^{-1}$ separation between the negative peak and the positive evidences the anharmonic nature of the vibrational potential of the AS$_{\text{COO}}$ mode. Note that the peaks observed in any 2DIR spectra do not contain the contact ion-pair transition since those appear at ~1580 cm$^{-1}$ (Figure 3.4) and ion-pair vibrational frequency assignment is in agreement not only with the peak position for the contact ion-pair formed by another carboxylate containing ion,[37] but also with theoretical studies.[54] Moreover, the peak at 1590 cm$^{-1}$ shows the expected increase in intensity with NaCl concentration, though it has a very small contribution in both cases (Figure 3.4.). In addition, the 2DIR spectra appears to show of fifth order signals in the region corresponding to the ν=2 to ν=3 transitions, which is assigned to fifth order and not a cascade signal,[55] due to the presence of the diagonal peak (Figure 3.4.). The presence of high order processes is not new and is likely to arise from the large transition dipole of the asymmetric stretch of carboxylate asymmetric stretch. However, it is expected that will have a small contribution to the overall signal.[55]

The time evolution of 2DIR shows that at short waiting times the 2DIR peaks are more elongated and tilted along the diagonal line ($\omega_t = \omega_\tau$, black line in the 2D plots of Figure 3.3.), and
as Tw increases the 2DIR peaks become rounder and less tilted along the diagonal. The change in the elongation and tilt of the peaks is due to the loss of correlation between pump and probe frequencies as a result of motions of the solvent molecules in the solvation shell of the acetate ion; i.e., spectral diffusion.[35] Interestingly, the rate at which the $\text{AS}_{\text{COO}}$ loses its correlation appears to be different in the two samples, as evidenced by the tilt of the 2D peaks which is still observed in the 2DIR spectrum at $T_w = 2.1$ ps of 6M NaCl sample, and is not clear in the 2DIR peaks of the acetate ion in $D_2O$.

Figure 3.3. 2DIR spectra as function of waiting time of sodium acetate in $D_2O$ (top) and in 6M NaCl (bottom) solution.
Figure 3.4. 2DIR spectra of acetate at larger frequency windows, showing that the main peaks do not contain the contact ion-pair transition.

3.4. Discussion

The FTIR absorption spectra of the $\text{AS}_{\text{COO}}$ mode of the acetate ion in $\text{D}_2\text{O}$ and in NaCl solutions (Figure 3.1) is not well modeled with two Voigt profiles, which is in agreement with a previous report.[31] As seen in the FTIR spectra, the derived central frequency of the $\text{AS}_{\text{COO}}$ mode is statistically the same for the two solutions (Table ). The results indicate that the interaction between acetate and sodium ions is very weak even at a 6M NaCl concentration, where the ratio of sodium to acetate ions is $\sim$8:1. The weak interaction is also evidenced by the lack of a noticeable contact ion pair peak in the linear IR spectra, which is only barely noticeable in the 2DIR spectra (Figure 3.4). In addition, the lack of formation of contact ion pairs by the acetate ion is also in agreement with a previous study.[29]
Table 3.1. Parameters derived from the FTIR spectra of sodium acetate and azide in water and NaCl solution.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Parameter</th>
<th>D$_2$O</th>
<th>6M NaCl</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetate</td>
<td>$\omega_0$ (cm$^{-1}$)*</td>
<td>1561.3 ± 0.1</td>
<td>1561.4 ± 0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Acetate</td>
<td>FWHM (cm$^{-1}$)**</td>
<td>38.6 ± 0.5</td>
<td>36.4 ± 0.5</td>
<td>-2.2 (-6%)</td>
</tr>
<tr>
<td>Azide</td>
<td>$\omega_0$ (cm$^{-1}$)*</td>
<td>2042.7 ± 0.1</td>
<td>2046.7 ± 0.1</td>
<td>4.0 (0.2%)</td>
</tr>
<tr>
<td>Azide</td>
<td>FWHM (cm$^{-1}$)**</td>
<td>17.1 ± 0.5</td>
<td>21.4 ± 0.5</td>
<td>4.3 (25%)</td>
</tr>
</tbody>
</table>

*Computed by fitting with a Voigt profile.

**Derived directly from the normalized FTIR.

Similar to the central frequency, the full width at half maximum (FWHM) of the AS$_{\text{COO}}$ band remains fairly constant when the solution has large amounts of NaCl (Table 3.1.). While the slight difference in the width of the band might be real, it only represents a change of less than 6% with respect to the D$_2$O solution. To verify that the bandwidth of the AS$_{\text{COO}}$ band is particularly different from other ions, the change in asymmetric stretch mode is compared with that of the azide ion (N$_3^-$). Note that the azide ion was selected due to the similarity of the normal mode; i.e., asymmetric stretch involving three atoms. In addition, the azide ion has a B-coefficient of -0.014 M$^{-1}$, which is similar to that of the chloride ion (B = -0.014).[56] Thus, it is not expected that the azide ion will perturb significantly the water or salt solution structures.[33, 34]

In contrast with the acetate ion, FWHM and central frequency of the N$_3^-$ asymmetric stretch of the azide ion show a ~4 cm$^{-1}$ blueshift and 25% bandwidth when the concentration of sodium and chloride ions is set to 6M, displaying the expected sensitivity of the ion to changes in the concentration of ions in the water solution. In addition, the lack of change in the central frequency of the AS$_{\text{COO}}$ of the acetate ion suggests that the carboxylate group of acetate maintains a similar interaction with the solvent in both D$_2$O and NaCl solutions. The lack of change in bandwidth of the AS$_{\text{COO}}$ band points to an unexpected similarity in the vibrational dynamical components giving rise to the lineshape of the acetate AS$_{\text{COO}}$. 
The semi-classical theory predicts that the FTIR lineshape depends on the vibrational lifetime ($T_{10}$), rotational diffusion ($D$), and the FFCF through its lineshape function ($g(t)$). The mathematical expression of the FTIR lineshape is given by:

$$S(\omega) \propto Re \int_0^{\omega_0} e^{i(\omega-\omega_0)t} e^{-\tau/2T_{10}} e^{-2Dt} e^{-g(t)} dt,$$  \hspace{1cm} (1)

where $\omega_0$ is the transition frequency and $g(t)$ is the double integral of the frequency-frequency autocorrelation function (FFCF); i.e., $g(t) = \int_{t}^{t} \int_{0}^{t} d\tau' d\tau'' < \delta \omega_{01}(\tau'') \delta \omega_{01}(0) >$. The analytical form of the FTIR lineshape and the striking similarity in the FWHM of the AS$_{\text{COO}}$ could indicate the change of two or more of its parameters in opposite directions such that the total effect is cancelled out. However, the vibrational lifetime derived from the waiting time dependence of the 2DIR spectra shows that the $T_{10}$ of the AS$_{\text{COO}}$ does not change significantly between the two samples (Figure 3.5). Note that the $T_{10}$ values are in agreement with a previous study.[31] It is also possible that the lack of change in the lineshape width is caused by a compensation in the rotational diffusion ($D$). However, the extremely short lifetime of the vibrational transition does not allow us to measure a reliable value of $D$. To discard this effect, the $D$ value of another acetate ion (trifluoroacetate)[37] with a slightly longer $T_{10}$ is used. In this case, the reorientational motion of the AS$_{\text{COO}}$ of trifluoroacetate ($\tau_c = 1/6D = 4.3$ ps) reveals that the rotation diffusion only accounts for a very small percentage of the total lineshape width (~1 cm$^{-1}$). Furthermore, theoretical results from the AIMD simulation support a slow decay of the orientational correlation function (see below, Figure 3.6, and Table 3.2). Another possibility arises from a similarity in all the parameters of the Eqn. (1) for both the D$_2$O and 6M NaCl acetate solutions. However, as previously mentioned the dynamics of the FFCF is not the same in both samples. Thus, it is likely
that the similarity in the lineshape width is caused by the compensation of the parameters within the FFCF. To assess this last possibility, all the FFCF parameters are required.

Figure 3.5. The vibrational lifetime derived from the waiting time dependence of sodium acetate in D2O (left) and in NaCl (right).

Figure 3.6. Dipole reorientation dynamics of the AS\textsubscript{COO} computed from the AIMD. The exponential characteristic decay times were found to be 8.8 ± 0.1 ps and 8.2 ± 0.1 ps for water and NaCl solutions, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_1$</th>
<th>$\tau_1$ (ps)</th>
<th>$A_2$</th>
<th>$\tau_2$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.22±0.01</td>
<td>0.17±0.01</td>
<td>0.81±0.01</td>
<td>8.20±0.01</td>
</tr>
<tr>
<td>NaCl solution</td>
<td>0.16±0.01</td>
<td>0.06±0.01</td>
<td>0.89±0.01</td>
<td>8.81±0.01</td>
</tr>
</tbody>
</table>
The decorrelation times of the FFCF of the $\text{AS}_{\text{COO}}$ are extracted from the $T_W$ evolution of the 2DIR spectra. Here, the characteristic times of the FFCF for both samples were derived from the inverse of slope of the zero contour line separating the negative and positive peaks (Figure 3.7) because it has been shown that this spectral feature correctly describes the dynamics of the FFCF.[57, 58] Note that the inverse slope was calculated in a range of ±10 cm$^{-1}$ of the central frequency. The time dependence of the inverse slope for the $\text{AS}_{\text{COO}}$ in water and salt solutions is shown in Figure 3.8. The inverse slope presents different values at short waiting times for the $\text{AS}_{\text{COO}}$ in water (~0.15 at $T_W = 0.15$ ps) and in 6M NaCl solution (~0.25 at $T_W = 0.15$ ps) indicating an increase in the contribution of inhomogeneous part of FFCF with addition of NaCl.[59] This increment cannot be due to a change in the vibrational lifetime ($T_{10}$) of the acetate ion in both solutions since they are very similar (Figure 3.5). In addition, the inverse slope decreases to ~0.04
at the longest waiting time measured ($T_W = 2.1$ ps) for acetate in D$_2$O, while the value for the 6M NaCl sample at the same waiting time is $\sim$0.1. The change in the inverse slope at longer waiting times evidences the rise of a slow dynamical component with increasing amounts of sodium chloride in the solution.

![Figure 3.8](image)

Figure 3.8. Inverse of slope vs. waiting time ($T_W$) for the asymmetric stretch of sodium acetate (top panel) and azide (bottom panel). Black filled squares and open triangles correspond to the experimental inverse slope of the ions in water and NaCl solutions, respectively. The red line represents its exponential decay fitting as described in the text. Note that the first data point at $T_W = 0$ fs is excluded from the fitting due to the influence of non-resonance signals from the sample and sample cell components.

The waiting time evolution of the inverse of slope for both water and salt solutions were modeled with an exponential decay function of the form: $f(t) = y_0 + Ae^{-\frac{t}{\tau_1}}$, where $y_0$ is the offset, $A$ is the amplitude of the dynamical component, and $\tau_1$ its characteristic time. The parameters of
the fitting are listed in Table 3.3. Interestingly, the only observed decay time ($\tau_1$) is ~1.2 ps, irrespective of the salt concentration, and is on the same timescale as the FFCF decay time of the aqueous trifluorocarboxylate ion (~0.8 ps).[37] It was previously established that the picosecond characteristic time of the FFCF is related to the hydrogen bond network reorganization dynamics around the carboxylate group of the acetate ion.[37] The similarity between the decay time in both D$_2$O and 6M NaCl solutions suggests that the carboxylate group of acetate ion must be sensing the same type of water dynamics in both solutions. While it is possible that the NaCl does not influence the hydrogen bond network reorganization dynamics of water, previous experimental studies have demonstrated definitively that the water slow down its dynamics in the presence of salts like NaBr.[60] Furthermore, the inverse slope derived from the 2DIR of sodium azide in the same conditions (Figure 3.9) shows a factor of two in slowdown of the FFCF dynamics of the N$_3^-$ asymmetric stretch mode (Table 3.3), which corroborates the expected slowdown in the motions of water. Overall the FFCF modeling agree with the most likely scenario for explaining the similarity in the AS$_{\text{COO}}$ lineshape where the changes in the lineshape function ($g(t)$) are self-compensated by the weight and contribution of the different FFCF components, though the component with a characteristic time of ~1.2 ps remains unchanged in the two samples.
The characterization of all the parameters of the FFCF is performed by finding the values that correctly predict the experimental FWHM of the $A_{SO}$ (Table 3.3), as well as the inverse slope at 0.15 ps and 2.1 ps (Figure 3.9) using the response function representation of the third order non-linear signal[61] in a similar manner as the studies in Ref. [62] and [37]. The proposed FFCF has a functional form based on the standard Kubo formalism,[63]

$$\text{FFCF}(t) = \frac{\delta(t)}{T_2^*} + \Delta_1^2 e^{-t/\tau_1} + \Delta_2^2,$$  (3)

where $T_2^*$ represents a homogeneous dephasing component, $\Delta_1$ and $\tau_1$ are the amplitude and decay time of a component which cannot be described by either inhomogeneous or homogeneous limit,
and $\Delta_2$ is the amplitude of an inhomogeneous component.[35] The results of the modeling (Table 3.4) show that the acetate ion in D$_2$O only requires a homogeneous component and a Kubo function, while the acetate ion solution in 6M NaCl requires an additional inhomogeneous component to correctly describe the three experimental parameters. It is interesting to observe that the homogeneous component becomes increasingly slow with the addition of salt, while the amplitude of the fluctuation of the ~1.2 ps component remains unchanged. Moreover, the appearance of an inhomogeneous component could indicate the presence of slower water dynamics which is likely to arise from the transformation of a fast dynamical component (originally represented by a homogeneous contribution), to an extremely slow component (given by the inhomogeneous contribution). However, it is also possible that the band is composed of two different transitions arising from solvent separated ion-pairs as it will be shown in the later sections of the manuscript.

Table 3.4. Lineshape function parameters derived from modeling the FWHM of the IR spectrum as well as the inverse of the slope at 0.15 ps and 2.1 ps.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\omega_{10}$ (cm$^{-1}$)</th>
<th>$\Delta_1$ (ps$^{-1}$)</th>
<th>$\Delta_2$ (ps$^{-1}$)</th>
<th>$T_2^*$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_2$O</td>
<td>1561</td>
<td>1.6 ± 0.1</td>
<td>--</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>NaCl$^1$</td>
<td>1561</td>
<td>1.6 ± 0.1</td>
<td>0.9 ± 0.1</td>
<td>2.0 ± 0.1</td>
</tr>
<tr>
<td>NaCl$^2$</td>
<td>1557</td>
<td>1.6 ± 0.1</td>
<td>--</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>NaCl$^2$</td>
<td>1565</td>
<td>1.6 ± 0.1</td>
<td>--</td>
<td>1.5 ± 0.1</td>
</tr>
</tbody>
</table>

$^1$ Modeled with one transition
$^2$ Modeled with two transitions

To understand the molecular processes that give rise to the observed vibrational dynamics, the solvation of the acetate ion was further studied by AIMD simulations. The local environment surrounding the acetate ions in the two different solutions is first evaluated from the radial distribution function (RDF) between the carbon atom of the carboxylate group and the oxygen atoms of water (Figure 3.10). The computed RDFs show a complete overlap up to 4.15 Å indicating not only that the acetate ion has the similar amount of water molecules in its first
solvation shell, but also that the sodium and chloride ions do not perturb significantly the acetate first solvation shell. Moreover, the radial distribution function for the acetate ion in water is found to be in agreement with previous theoretical study.[64] In addition, the RDF shows that the acetate ion in water has a second and third solvation shells, as evidenced by the two peaks at ~5 Å and ~7 Å. In contrast, at high NaCl concentration the structure of the second and third solvation shells are significantly affected, as seen by the lower amplitude of the peak ~5 Å and by the lack of a third peak in the RDF. The numbers of water molecules in the first solvation shell were computed to be ~7.0 and ~6.4 for water and 6M NaCl solutions, respectively. This result indicates that acetate forms on average three hydrogen bonds with each of its oxygen atoms which is consistent with the observation of a previous study.[64]

![Figure 3.10. Radial distribution function between carbon in carboxyl group and oxygen in water molecule in sodium acetate water solution (black line) and sodium acetate NaCl solution (red open circles).](image)

The FFCF dynamics of the acetate ion in both solutions was also derived from the AIMD simulations (Figure 3.12). The computed FFCFs (see theoretical methods) shows a dynamic process with at least two different time scales. Interestingly, the variance of the frequency fluctuations remains almost invariant with the addition of large quantities of sodium and chloride ions. The characteristic times of the FFCF dynamics were quantified by modeling its time
dependence with a sum of three exponential decay functions; i.e., $\text{FFCF}(t) = \sum A_i^2 e^{-\frac{t}{\tau'_i}}$. The parameters from the fitting are shown in Table 3.4. Similarly to the experimental FFCF, $\tau'_3$ is assigned to the global structural rearrangement of hydrogen bond network arising from rotational jumps and hydrogen bond making and breaking.[60, 65] Notably, the slow characteristic time of the FFCF ($\tau'_3$) remains fairly unchanged in both the water and salt solutions which is in reasonable agreement with experimental results. The other two fast correlation times ($\tau'_1$ and $\tau'_2$) are related to the water molecule libration motions[60, 66] and to the internal bending and stretching motions of water molecules.[60, 67] Moreover, the presence of two fast dynamical components ($\tau'_1$ and $\tau'_2$) supports the needed homogeneous component in the modeling of the experimental FFCF, as previously described.

The simulated FFCF does not capture the presence of the slow component seen experimentally, which could be due to the small time window (~50 ps) obtained from the AIMD. However, the FFCF computed from classical MD simulations also does not predict the slow dynamical component on a time window of ~450 ps (Figure 3.11), which allows us to discard the temporal sampling as the cause of the lack of a slow component. Thus, it is likely that the slow component arises from two slowly exchanging configurations of the hydrated acetate ion. While one possibility could come from slow solvent exchange due to the overlapping solvation shells between acetate and sodium ions, the hydrogen bond dynamics between the acetate ion and water molecules does not seem to be affected by the salt concentration (see below). Thus, it is likely that the effect is caused by the presence of solvent separated ion pairs (SIP). In a SIP, the central frequency of the $\text{AS}_{\text{COO}}$ could be shifted by a water mediated charge transfer between sodium and acetate ions (electronic effect). In this case, SIPs should have a slightly different $\text{AS}_{\text{COO}}$ central
frequency, which will essentially split the band and give rise to the observed inhomogeneous component of the FFCF (Table 3.4). In addition, the presence of two transitions could explain why the FWHM for the AS\textsubscript{COO} (~30 cm\textsuperscript{-1}, Table 3.5) derived from the theoretical FFCF is narrower in both water and salt solutions when compared to the experimental value (Table 3.1) since the calculation assumes a single transition when computing the FFCF.

![Figure 3.11. FFCF computed from the classical MD simulations for 45 temporal windows of 10 ps each.](image)

The simulation of the temporal evolution of 2DIR spectra using a pair of transitions (Table 3.4) reproduces the experimental slope values and the FWHM of the AS\textsubscript{COO}. However, the simulation also requires a frequency difference of ~9 cm\textsuperscript{-1} between the band maxima. The calculated split should shift the central frequency of the transition, but this effect is not observed in the FTIR. However, it is also possible that there is an accidental cancellation of effects from ion pairing and the change in the dielectric constant of the medium due to the addition of the salt. It is important to note that this effect will not be capture by calculating the FFCF from the theory because if the shift in the frequency arise from electronic effects, such as charge transfer, it will require the inclusion of both transitions with their corresponding gas phase frequencies and the identification of these species in the trajectory to compute the theoretical FFCF. The determination
of the involvement of such species will require a thorough investigation and vibrational characterization of the species formed during the MD simulation, which is beyond the scope of this paper.

The presence of a second transition is an interesting topic on its own, but it does not explain the picosecond FFCF dynamics of the acetate ion and its lack of sensitivity to salt concentration. The AIMD simulations allow us to discard any possible effect of the randomization of the orientational distribution of the carboxylate group as a source of the fast decorrelation of the FFCF.[68] To this end, the anisotropy of the AS$_{\text{COO}}$ is computed from the second order correlation function of the orientation of the AS$_{\text{COO}}$ transition dipole $R(t) = 2/5\langle P_2[u(0) \cdot u(t)]\rangle$, where $u(t)$ is the transition dipole and is represented here by the unit vector joining the two oxygen atoms of the carboxylate group, $P_2$ is the second order Legendre polynomial, and the angle brackets indicate the ensemble average. The computed anisotropy (Figure 3.6 and Table 3.2) shows a very slow decay with a time constant of ~8 ps in both NaCl and D$_2$O. The result indicates that the reorientation-induced contribution plays little to no role in the FFCF.
Figure 3.12. Autocorrelation function of the frequency fluctuations (FFCF) computed from the AIMD and the frequency map. Top and bottom panels correspond to sodium acetate in water and in NaCl solution, respectively. Black open squares correspond to the computed FFCF and the red line to the fitting with a sum of exponential functions as described in the text. While the plots highlight the slow decay times, the insets show the whole correlation function.

Table 3.5. Parameters from fitting of the theoretical FFCF and HBCF of sodium acetate solutions.

<table>
<thead>
<tr>
<th>Metric</th>
<th>Sample</th>
<th>$\Delta_1$ (ps$^{-1}$)</th>
<th>$\tau_1$ (fs)</th>
<th>$\Delta_2$ (ps$^{-1}$)</th>
<th>$\tau_2$ (fs)</th>
<th>$\Delta_3$ (ps$^{-1}$)</th>
<th>$\tau_3$ (fs)</th>
<th>FWHM (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FFCF</td>
<td>water</td>
<td>1.7±0.1</td>
<td>6.8±0.2</td>
<td>1.5±0.1</td>
<td>99±2</td>
<td>1.5±0.1</td>
<td>2190±50</td>
<td>30.1±0.3</td>
</tr>
<tr>
<td>FFCF</td>
<td>NaCl</td>
<td>1.8±0.1</td>
<td>6.9±0.3</td>
<td>1.3±0.1</td>
<td>116±3</td>
<td>1.8±0.1</td>
<td>1530±30</td>
<td>33±1</td>
</tr>
<tr>
<td>HBCF (acetate-water)</td>
<td>water</td>
<td>1.05±0.01</td>
<td>5.5±0.1</td>
<td>0.19±0.01</td>
<td>85±3</td>
<td>0.07±0.01</td>
<td>590±20</td>
<td></td>
</tr>
<tr>
<td>HBCF (acetate-water)</td>
<td>NaCl</td>
<td>1.03±0.01</td>
<td>5.7±0.1</td>
<td>0.16±0.01</td>
<td>94±4</td>
<td>0.09±0.01</td>
<td>800±20</td>
<td></td>
</tr>
<tr>
<td>HBCF (water-water)</td>
<td>water</td>
<td>0.68±0.01</td>
<td>5.1±0.1</td>
<td>0.26±0.01</td>
<td>76±2</td>
<td>0.20±0.01</td>
<td>520±5</td>
<td></td>
</tr>
<tr>
<td>HBCF (water-water)</td>
<td>NaCl</td>
<td>0.68±0.01</td>
<td>5.2±0.1</td>
<td>0.22±0.01</td>
<td>71±2</td>
<td>0.13±0.01</td>
<td>1120±20</td>
<td></td>
</tr>
</tbody>
</table>
The molecular mechanism behind the lack of change of the ~1-2 ps component of the calculated and measured FFCF with the addition of salt was studied by computing the hydrogen bond dynamics of the acetate and water from the AIMD simulation. The number of hydrogen bonds between acetate and water was used in this case because it has been previously shown that the frequency fluctuations in the acetate ion are dominated by a rearrangement of the hydrogen bonds around the oxygen atoms of the carboxylate. For this purpose, the distance between oxygen atoms of the ion acetate and water molecules was used as parameter to define the existence of a hydrogen bond.[69] Figure 3.13 shows the correlation functions of the number of hydrogen bonds (HBCF) between the acetate ion and water molecules for both solutions. It is clear that the hydrogen-bond dynamics between the acetate ion and water molecules are very similar in water and salt solutions. The modeling of the HBCF with the sum of three exponential decays of the form: 

$$\text{HBCF}(t) = \sum A_i e^{-\frac{t}{\tau_i}},$$

reveals the presence of two short characteristic times ($\tau''_1$ and $\tau''_2$) with no obvious difference for both samples, and a long characteristic time ($\tau''_3$) that increases from ~600 fs in D$_2$O to ~800 fs in NaCl (Table 3.5). Although the change in $\tau''_3$ indicates that the sodium and chloride ions alter the dynamics of hydrogen bond between the acetate ion and water, the observed change is not large. Interestingly, a similar analysis of the HBCF among water molecules outside of the solvation shell (Figure 3.13) shows an analogous picture for $\tau''_1$ and $\tau''_2$, but completely different for the long correlation time $\tau''_3$. Again, the modeling of the water-water HBCF with a sum of three exponential functions (Table 3.5) reveals that the third decay time ($\tau''_3$) has a large increase in its value when the solution has a significant amount of sodium and chloride ions. In contrast, the presence of ions does not seem to affect the other two decay times ($\tau''_1$ and $\tau''_2$). The difference between the acetate-water and water-water HBCF confirms the known
slowdown of water hydrogen bond dynamics with the addition of NaCl.[60] In addition, it verifies that the invariance of the acetate-water hydrogen bond in the presence of large quantities of sodium and chloride ions is not an artifact of the AIMD. Moreover, it further supports of our experimental observation in which the FFCF dynamics remains unchanged in solutions saturated with NaCl, but does not provide the molecular mechanism behind this effect.

Figure 3.13. Hydrogen bond autocorrelation function. Top panel shows the HBCF between acetate and water molecules and bottom panel displays the HBCF between water molecules outside of solvation shell. Solid black and red dashed lines correspond to acetate in water and in NaCl solutions, respectively. While the plots highlight the slow decay times, the insets show the whole correlation function.

The simplicity of the acetate ion allows us to uncover the molecular mechanism responsible for the interesting solvation shell dynamics of the ion. Acetate has only one substituent that can affect the solvation shell of its COO− group; i.e., its methyl group. It is well known that the energetics of the rotation of methyl groups is well within thermal energy.[70-72] Thus, it is not
surprising that the acetate ion controls its solvation shell by the thermal rotation of its methyl group. To test this hypothesis, the correlation between the number of hydrogen bonds formed between water and one oxygen atom of the acetate ion and the HCCO dihedral angle of acetate is computed. The correlation numbers between these two variables are found to be ~ -0.6 for both water and salt solutions (Figure 3.13) which indicates that the HCCO dihedral angle directly affects the hydrogen bonding occurring at the carboxylate group. The dynamics of the dihedral angle is derived from the correlation function: 

\[ C(t) = \langle \cos[\theta(\tau) - \theta(\tau + t)] \rangle_{\tau}, \]

where \( \theta \) is the dihedral angle and \( t \) is the residence time in a single dihedral angle conformation (see Figure 3.14).[73] The characteristic times of the dynamics computed by modeling the data with the sum of two exponential decays reveals the presence of two residence times: one on the order of ~100 fs and the other larger than 1 ps (Table 3.6). While the values of the characteristic times might not be very precise due to the short time window used to evaluate this correlation function, they still show that the rotation dynamics of the methyl group has a comparable time scale to that observed for the FFCF. The fast rotational dynamics of the methyl group as well as the observed correlation between the number of hydrogen bonds in the carboxylate group and the dihedral angle strongly supports the proposed molecular mechanism in which the rotation of the methyl group controls the structure and dynamics of the acetate first hydration shell. The observed mechanism has multiple implications in the properties of the carboxylate group. For example, it provides a molecular framework for describing why carboxylate groups do not tend to favor the formation of contact ion pairs with alkali metals.
Figure 3.14. Dihedral autocorrelation function of HCCO. Top and bottom panel correspond the autocorrelation for water and NaCl solutions, respectively. Black line is the computed autocorrelation and the red dashed line is fitting with a sum of exponential decays. Inset show the number of hydrogen bonds in one oxygen atom of the carboxylate as a function of the HCCO dihedral angle.

Table 3.6. Exponential decay fitting \( f(t) = \sum A_i e^{-t/\tau_i} \) parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>( A_1 )</th>
<th>( \tau_1 ) (fs)</th>
<th>( A_2 )</th>
<th>( \tau_2 ) (fs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.0 ± 0.01</td>
<td>174 ± 2</td>
<td>0.06 ± 0.01</td>
<td>1760 ± 120</td>
</tr>
<tr>
<td>NaCl solution</td>
<td>0.90 ± 0.01</td>
<td>150 ± 2</td>
<td>0.22 ± 0.01</td>
<td>1320 ± 30</td>
</tr>
</tbody>
</table>

3.5. Summary

The solvation shell dynamics of acetate ion in D\(_2\)O and 6M NaCl solution was successfully studied by FTIR and 2DIR experiments. The linear IR spectroscopy of the acetate AS\(_{\text{COO}}\) mode revealed that its IR lineshape is not affected by the high concentration of sodium and chloride ions. In addition, the FFCF deducted from the photon echo experiments revealed a ~1 ps component
which is also not affected by the concentration of ions. A comparison with the effect on the asymmetric stretch of the azide ion showed that the lack of change in the \( \text{AS}_{\text{COO}} \) lineshape and FFCF dynamics is a particularity of the acetate ion. AIMD simulations confirmed that the hydration shell structure and dynamics of acetate ion is not affected by the presence of large quantities of ions, while substantial amounts of charged species produced a slowdown in the hydrogen bond dynamics of water molecules outside the acetate first hydration shell. Moreover, the FFCF and lineshape derived for the acetate \( \text{AS}_{\text{COO}} \) from AIMD simulations and a DFT-frequency map presented a reasonable agreement with the experiments, but they fail to explain the observed inhomogeneous components of the FFCF. Our results and modeling suggest that the inhomogeneous component could arise from the presence of solvent separated ion pairs. Finally, the computational modeling provided a molecular framework for understanding the vibrational spectra and dynamics of the acetate ion. In this case, the thermal rotation of the acetate methyl group (–CH\(_3\)) is found to be responsible for controlling the structure and dynamics of the water molecules in the first solvation shell. Our experiments provide the molecular basis for rationalizing why osmolytes and zwitterions containing the carboxylate group, such as betaine, avoid the formation of ion pairs and maintain their high water solvation number, even in solutions with high salt concentrations.

3.6. References


2. Lombard, J., *Once upon a time the cell membranes: 175 years of cell boundary research*. Biology Direct, 2014. 9: p. 32.


CHAPTER 4
AN AB INITIO MOLECULAR DYNAMICS STUDY OF THE SOLVATION STRUCTURE AND ULTRAFAST DYNAMICS OF LITHIUM SALTS IN ORGANIC CARBONATES: A COMPARISON BETWEEN LINEAR AND CYCLIC CARBONATES

4.1. Introduction

Lithium ion batteries with carbonate electrolytes have been extensively used in portable energy devices due to their advantages such as low cost, high energy density, and no memory effect. However, this technology still suffers from some drawbacks such as limited thermal stability and low efficiency compared to its theoretical value. In most current commercial lithium ion batteries, the electrolyte is composed of both a linear carbonate, such as dimethyl carbonate (DMC, Scheme 4.1) or ethyl methyl carbonate (EMC), and a cyclic carbonate, like ethylene carbonate (EC) or butylene carbonate (BC).[1] The mixture is needed to gain the best physicochemical properties of each solvent, namely, the high dielectric constant of the cyclic carbonate and the low viscosity of the linear carbonate. Previous studies have demonstrated that the solvent used in the electrolytes influences the battery performance through the ionic conductivity, which is determined by the solvation and diffusion of lithium ions (Li+),[2] and by forming the solid-electrolyte interphase, which avoids the degradation of the battery capacity.[3] In addition, it has been proven that the stability of lithium ion batteries can be improved by modifying the solvent composition of the electrolyte.[4, 5] Thus, to improve the overall battery

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stability and efficiency, the interactions among electrolyte components should be investigated and optimized.

![Scheme 4.1](image)

Scheme 4.1. Chemical structure of carbonates. Ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC). Dashed circle denotes the methylene and methyl carbons used for calculating the radial distribution functions.

Numerous studies have investigated the solvation structure and dynamics of lithium ion electrolytes using experimental methodologies, such as X-ray scattering,[6, 7] nuclear magnetic resonance,[8-12] Raman spectroscopy,[12-17] and linear and ultrafast infrared spectroscopy.[18-22] Similarly, several theoretical studies using different levels of theory have also been presented.[23-28] While it has been a long time since the physicochemical properties of cyclic and linear carbonates, such as dielectric constant, viscosity, and electrochemical stability, have been presented,[1] the molecular level description of the organic carbonate behavior is still scarce. In particular, some studies have focused on the mixture of cyclic and linear carbonate solutions using experimental and theoretical methods to obtain the composition and dynamics of the mixed solvation shell.[18, 28-30] However, due to the complexity of the system, namely, fast exchange of solvent molecules and different speciation of the ionic species, the knowledge derived from such systems has been rather limited. On the other hand, only a few studies have investigated the
differences of solvation structure and interactions between the two types of carbonate solutions.[31, 32]

Lately, there have been a significant number of studies using vibrational spectroscopy to study the solvation of Li+ in organic carbonates.[12-17, 31-34] In particular, some studies have used ultrafast IR spectroscopy to investigate the solvation structure and dynamics of Li+ in organic carbonates.[18, 20-22, 35] However, it appears that the ultrafast spectroscopy work has produced more contradictions than agreements. For example, the coordination number of lithium ion by carbonates has been found to be 4 by some of the ultrafast spectroscopic studies,[21, 22] while others predicted the coordination number of 2 and 6.[19, 35] Moreover, the disagreement in the Li+ solvation number is also found across vibrational spectroscopies, such as Raman[36, 37] and FTIR.[31] In addition, there have been contradictions in the ionic speciation of lithium ions and its counter ion in solutions of organic carbonates.[20, 31, 32, 35] For example, some studies have claimed that the majority of the lithium ions are found forming contact ion pairs (CIP),[35] whereas others predicted an speciation based majorly on solvent separated ion pairs (SSIP) and free ions for the same solutions.[20] Finally, one study predicted a fast solvent exchange of those organic carbonate in the first solvation shell of the lithium ion,[18, 19] while another study pointed out that the experimental signature assigned to solvent exchange arises from a vibrational energy transfer mechanism due to deformations of the solvation shell of the lithium ion.[21] In addition, this last work had shown a significant difference in the solvation shell dynamics between linear and cyclic carbonates which have opposing dynamical trends with lithium salt concentration.[21] As a consequence, further study is needed to disambiguate the interactions and motions of the molecular components in lithium salt solutions of linear and cyclic carbonates. To this end, we present here
a theoretical study based on ab initio molecular dynamics simulations. In particular, this theoretical study is focused on disambiguating the ultrafast processes and the molecular mechanism measured by the different ultrafast vibrational studies.

Molecular dynamics (MD) simulations of lithium salts in linear and cyclic carbonate solutions have been widely studied using classical potentials (GAFF [10, 38] and OPLS-AA [39]), modified or self-developed polarizable empirical potentials,[25, 29, 39-42] semi-empirical quantum mechanical potentials (PM7),[24] and ab initio-based potentials.[2, 4, 23, 28, 43-48] Although the number of studies is significant, the contradictions seen in the experiments are also observed in the theoretical work. For example, some studies show a coordination number of 6 for the lithium ion using classical MD simulations,[23, 40] whereas a tetrahedral structure with a coordination number of 4 for the lithium solvation shell in linear and cyclic carbonates was observed in all the ab initio studies,[2, 4, 23, 28, 43-48] PM7 calculations,[24] and the classical MDs with custom/modified force fields.[25, 29, 39, 42, 49] However, it has been demonstrated independently by Rick’s and Rempe’s groups that well-optimized polarizable or quantum-based well-modified or quantum models are required to accurately reproduce the solvation properties of the lithium ions in carbonates.[38, 39] These last studies might explain why classical MDs with off-the-shell potentials are likely to fail in properly describing the lithium ion solvation and speciation in organic carbonates.

The speciation of the lithium ion in organic carbonates has been also investigated theoretically. As with the solvent coordination number, the speciation predicted theoretically also showed inconsistencies among different studies. For example, classical MD shows a large population of CIP existing in lithium hexaflourophosphate solutions of ethylene carbonate.
In contrast, the potential energy surface for the lithium tetrafluoroborate in EC at CAM-B3LYP/6-31G(d) level suggests that SSIPs are the most energetically favorable species.[48] Another study using energy representation method for LiBF4 and LiPF6 in propylene carbonate (PC) and dimethyl carbonate (DMC) suggested that CIP is most energetically favorable species irrespective of the dielectric constant of the carbonate.[42] In addition, ab initio MD study predicted a lithium ion solvation energy as high as 140 kcal/mol in EC.[46] Interestingly, the solvent exchange between first- and second-solvation shell was studied by two groups using classical and quantum MDs. The solvent exchange was not observed within the 30 ps AIMD simulation containing LiPF6 in EC or PC,[2] but a classical MD predicted a fast exchange of molecules in the lithium first solvation shell.[18]

In the present work, ab initio molecular dynamics simulations (AIMD) based on density functional theory are used to investigate the solvation structure and dynamics of the lithium ion in both linear and cyclic carbonates. We have chosen AIMD because the electrons are treated quantum mechanically without the need of extra empirical parameters. This methodology has shown a significant predictive power on exploring chemical process that are difficult to probe experimentally.[50, 51] The AIMD simulations used here are based on the PBE functional, which has a proven record of accurately capturing the structure and dynamical properties of the lithium solvation shell as well as the other relevant reactions in carbonate-based electrolytes.[2, 23, 43, 51] However, the cost of such computation is currently exceedingly high and limits the possible time window. To avoid the sampling problems associated with the short time window investigated by the AIMD, the present study also used ab initio umbrella sampling (AIUS) to calculate the
potential of mean force (PMF) and their corresponding probability distributions involved in the processes of ion pairing and solvent exchange.

The paper is organized as follows. Section II discusses the theoretical methods. The results and discussion are presented in Section III, followed by Conclusions in Section IV.

4.2. Theoretical methods

4.2.1. Ab Initio Molecular Dynamics Simulations (AIMD)

The AIMD simulation was carried out with the CP2K package (ver 3.0).[52] The electronic structure was calculated via Quickstep module[52] using the PBE functional with the D2[53] dispersion scheme and the TZ2VP basis set, with Goedecker-Teler-Hutter (GTH) pseudopotentials.[54-56] Periodic boundary conditions were applied to all the systems, and the Nosé-Hoover thermostat was used to keep the temperature as a constant of 300 K with the temperature damping constant of 100 fs. Self-consistent field (SCF) convergence criterion was set to 5.0x10^-7 Hartree. The cyclic carbonate system was composed of 1 lithium ion (Li+), 1 hexafluorophosphate ion (PF_6^-), and 19 butylene carbonate (BC) molecules in a cubic box with a length of ~16 Å. Note that BC was selected because it is the only cyclic organic carbonate that could be studied directly using ultrafast IR spectroscopy.[21] In the case of the linear carbonate, the system was composed of 1 Li+, 1 PF_6^-, and 23 DMC molecules in a cubic box with a length of ~17 Å. In both cases, the box composition is representative of low concentration LiPF_6-carbonate solutions (i.e., c < 1M) because it has been observed that aggregates are not present at significant concentrations in these solutions.[20, 31, 57, 58]
To obtain the initial box, Li+ coordinated with 4 carbonates were firstly optimized by using Gaussian09.[59] Note that we have selected DMC molecules with cis-trans conformation because the stabilization energy is similar to those with a mixture of cis-cis and cis-trans conformations (Figure 4.1). In addition, it has been previously demonstrated that entropy does not play a significant role in the solvation energetics.[28] The optimized structure was then submerged in a box containing the rest of the carbonate molecules using Packmol.[60] The system with restraints in the positions of the four coordinated oxygens of the carbonyl in each carbonate underwent a 10 ns NVT, 10 ns NPT, and 15 ns NVT process using LAMMPS software package and OPLSAA force field.[61, 62] These first steps were required to assure the equilibration of the box while maintaining the correct solvation structure around Li+. In the case of linear carbonate, the \textit{cis-trans} isomers were used for coordinated linear carbonates, while the rest of the box was filled with \textit{cis-cis} DMC. The presence of different isomers of the linear carbonate was needed because it has been found that \textit{cis-cis} DMC has lower free energy,[31] whereas the solvation shell of Li+ complex significantly stabilize the \textit{cis-trans} conformer.[29, 31] The initial configurations for the AIMD simulations were obtained from the last 15 ns of the NVT MD. In the AIMD, the systems were equilibrated for \textasciitilde5 ps, and the production run was carried out in the NVT ensemble for another 200 ps. In each case, the time step of the AIMD was 0.5 fs.
Figure 4.1. Relative solvation energy calculated using PBE/6-31+G(d,p) in gas phase for Li+ containing different number of DMC cis-trans (DMCct) and cis-cis (DMCcc) conformers in the solvation shell.

4.2.2. Ab Initio Umbrella Sampling (AIUS)

The potential of mean force along different reaction pathways involving ion pair formation and solvent exchange was obtained at the ab initio level using the umbrella sampling method. This methodology allowed us to evaluate the convergence of the computationally demanding AIMD as well as estimate the probability distributions and energetics of species with a low probability of occurring. The reaction coordinate in AIUS simulations was set as the distance between Li+ and the phosphorus atom of the counterion for calculating the ion pairing and between Li+ and a carbonyl oxygen for solvent exchange. Approximately 20 windows were employed in each AIUS simulation. Harmonic potentials were adopted as the biasing constraint in the form of

\[ U_i(x) = \frac{1}{2} k(x - x_i)^2, \]

where \(i\) represents the \(i^{th}\) biasing potential, spring constant \(k\) varies from 10.04 kcal/mol/Å\(^2\) to 25.1 kcal/mol/Å\(^2\), and \(x_i\) is the reaction coordinate of the center of each harmonic biasing potential. Initial configurations with a reaction coordinate of ~7 Å were taken from the snapshots of the
AIMD simulation, and then driven from ~7 Å to ~2 Å (forming process) by sequentially applying the ~20 biasing potentials for windows of ~14 ps each. In each window, the first 2 ps were discarded due to system equilibration. A similar method was used to simulate the breaking process, but in this case, the system was driven using a reaction coordinate that was varied from ~2 Å to ~7 Å. The weighted histogram analysis method (WHAM) was used to unbias the system and obtain the free energy of the proposed reaction coordinate (PMF).[63-66]

4.3. Results and discussion

4.3.1. Cation solvation

The geometry and composition of the solvation shell structure as a function of the molecular structure of the organic carbonate were first investigated by measuring the radial distribution functions (RDF, g(r)) and angular and distance distributions from the canonical AIMD. The g(r) and the integrated g(r) between Li+ and the carbonyl oxygen (O_C) of the carbonate (Figure ) shows a very sharp first peak located at 1.95 Å irrespective of the carbonate structure, which is in agreement with previous experimental and computational results.[2, 24, 44] A second maximum located at ~7.5 Å, barely noticed in the g(r), indicates a separation of ~5.5 Å between first and second solvation shell. A coordination number of 4 is deduced from the integrated g(r) at a distance of 4 Å validating the tetrahedral solvation structure of lithium in both BC and DMC solutions observed experimentally.[21] The presence and location of the second solvation shell is in agreement with previous studies.[23, 67] As expected, the g(r) between the lithium and carbonyl carbon (C_C) shows the same results as between the Li+ and O_C (Figure 4.2(b)); i.e., an overlapped lineshape with a coordination number of 4. However, the first maximum in the RDF of Li+-C_C is located at 2.95 Å. The presence of the maxima at ~3 Å implies that the carbonyl groups are not
pointing directly towards Li+, but they are slightly tilted. In addition, RDFs of Li+-C<sub>c</sub> of BC and DMC samples showed 2 peaks and 1 peak in the range of 4-8 Å, respectively. The presence of a second peak in the g(r) of Li+-C<sub>c</sub> is not a contradiction between the two RDFs, but an indication of the intercalation of BC molecules in the first solvation shell of Li+ as will be discussed later.

Figure 4.2. RDF profiles and integral of g(r) of Li+ in BC (black solid line) and in DMC (red dashed line). (a) g(r) between Li+ and carbonyl oxygen, (b) g(r) between Li+ and carbonyl carbon, (c) g(r) between Li+ and methyl or methylene carbon.

The RDF between lithium and the carbon of methyl group of DMC, and the methylene group of the cycle in BC were also calculated (Figure 4.2(c) and Scheme 4.1). In contrast to the RDF of the oxygen and carbon atoms of the carbonyl group, the RDFs of carbon of the methyl
and methylene group of the carbonates show a striking difference between DMC and BC. In the case of DMC, the RDF shows a first peak with multiple shoulders and a maximum at 4.6 Å and a featureless second peak more asymmetric at 8.0 Å. Two peaks are also observed in the RDF of BC, but they are both relatively featureless and located at 5.1 Å and 9.5 Å. In addition, both DMC and BC RDF show a first minimum at ~6 Å and ~7 Å, respectively, which indicates the presence of a defined first solvation shell. The differences between BC and DMC account for the existence of different methyl groups in DMC due to the presence of the cis-trans isomer (Figure 4.1) that are not present in the coordinated BC molecules, while the peak positions arise from the different molecular size of BC and DMC.

The integral of the g(r) shows that there are 7 methylene groups of BC and 12 methyl group of DMC within the first solvation shell of lithium. The results indicate that the first solvation shell of BC contains 7 molecules of the carbonate, whereas DMC has 6 molecules of the carbonate in the same location. While this result appears to contradict the RDF of the carbonyl atoms, the presence of more than 4 molecules in the first solvation shell demonstrates that groups of the molecules in second solvation shell insert and/or intercalate into the first solvation shell. Note that intercalation is defined here as the molecule being located within the first solvation shell, while insertion corresponds to parts of the solvent molecule being buried in the first solvation shell. To differentiate between intercalation and insertion within the first solvation shell the RDF of the methyl and cyclic methylene group of the carbonates is decomposed between carbonate that have or do not the carbonyl oxygen solvating Li+. The result shows that the methylene group of BC molecules not having the carbonyl solvating Li+ are in closer proximity to Li+ than those corresponding to carbonates solvating Li+. In contrast, the methyl groups of DMC are further away
than the closest methyl groups of carbonates solvating Li+. Thus, there are three BC molecules intercalating into the first solvation shell, but the extra DMC molecules are inserting parts of the molecule into the first solvation shell. To visualize the observed intercalation process, a “representative” snapshot of the AIMD trajectory, illustrating the composition of the first peak in the RDF, is shown in Figure 4.3.

![Figure 4.3](image)

Figure 4.3. RDF between Li+ and DMC methyl or BC methylene carbon. Left and right panels correspond to BC and DMC, respectively. The solid black line corresponds to all groups, the dashed red line to those groups of carbonates coordinating Li+, and the dotted blue line to carbonates not directly coordinating Li+. Snapshots on each side of the panel illustrate the intercalation and inserting processes.

The intercalation in BC comes from the strong dipole-dipole interaction as a result of its high dielectric constant, leading to a more organized and rigid solvation structure in BC than in DMC. This result explains the slower(faster) solvation dynamics at lower(higher) Li+ concentration observed in the previous 2DIR study,[21] due to a decrease(increase) of the number of intercalated carbonate molecules when the lithium concentration is increased(decreased). The
The observation of BC intercalation is also in agreement with the previous Raman and NMR studies.[9, 68]

The RDFs show that BC and DMC have different solvation structures. To study the effect of the molecular structure of the carbonate on the structural arrangement of the Li+ tetrahedral solvation shell, the order parameter:

\[ q = 1 - \frac{3}{8} \sum_{j=1}^{3} \sum_{k=j+1}^{4} \left\{ \cos(\phi_{jik}) + \frac{1}{3} \right\}^2, \]

was used to measure how tetrahedral the solvation structure formed by the carbonate molecules is. In this order parameter, \( \phi_{jik} \) is the angle between the \( j \) and \( k \) vertices and the center of the tetrahedron “i”.[69] For this order parameter, \( q \) is unity when the structure is strictly tetrahedral and \( q \) is zero when the four surrounding objects are randomly positioned.[69] The distribution of the \( q \) for \( OC \) in BC and DMC show very similar single distributions with extensive overlap in the whole \( q \) range (Figure 4.4) and same mean value (Table 4.1). The mean values of the \( q \) distributions demonstrate that the four \( OC \) form a tetrahedral structure around Li+, which is close to a perfect tetrahedron. A similar picture emerges from the \( q \) distribution of the carbon atom of the carbonyl group (Figure 4.4). However, the \( q \) distributions of \( CC \) are less tetrahedral than \( OC \) since their average is lower (Table 4.1), but is still fairly tetrahedral.
Figure 4.4. Distributions and autocorrelation functions of the tetrahedral parameter $q$ for BC (black solid line) and DMC (red dashed line) samples. Top and bottom panel correspond to coordinated carbonyl oxygens ($O_C$) and coordinated carbonyl carbon ($C_C$). Inset show the distribution function.

The dynamics of the first solvation shell is derived from the autocorrelation function of the $q$ factor defined as: $\langle \delta q(t) \delta q(0) \rangle$, where $\delta q(t) = q(t) - \langle q \rangle$. The autocorrelations of $q$ for the oxygen atoms show a very similar time evolution for both carbonates (i.e., a very fast process followed a slower one) with a similar decorrelation exponential times for both carbonates (Figure 4.4 and Table 4.1). The autocorrelation demonstrates that the motions of the coordinated oxygens around lithium ions are very similar in both systems. In contrast, the autocorrelation function of $q$ for $C_C$ exhibits a significant difference between BC and DMC. In this case, much faster decorrelation dynamics is observed for DMC compared to BC, which is evidenced in the characteristic times of 20 ps and 2 ps for BC and DMC, respectively. Notably, a similar timescale has been deduced from previous 2DIR experiments on similar systems.[21]
<table>
<thead>
<tr>
<th>Geometrical factor</th>
<th>Sample</th>
<th>BC</th>
<th>DMC</th>
</tr>
</thead>
</table>
| q of O
| <q>                       | 0.90   | 0.90  |
| \(\tau\) (ps)            | ~2     | ~2    |
| q of C
| <q>                       | 0.81   | 0.81  |
| \(\tau\) (ps)            | ~20    | ~2    |
| Li-O\(\text{C}\) distance| \(<d>\) | 2.03  | 2.04  |
| \(\tau\) (ps)            | ~1.8   | ~1.3  |
| O\(\text{C}\)-Li-O\(\text{C}\) angle| \(<\theta>\) | 108.8 | 109.2 |
| \(\tau\) (ps)            | ~2.0   | ~2.5  |
| Li-O\(\text{C}\)-C\(\text{C}\) angle| \(<\theta>\) | 132.9 | 134.4 |
| \(\tau\) (ps)            | ~5.0   | ~2.6  |
| C\(\text{C}\)-Li-C\(\text{C}\) angle| \(<\theta>\) | 104.8 | 108.4 |
| \(\tau\) (ps)            | ~22    | ~6    |
| FFCF from exp.            | \(\tau\) (ps) | 12.8±0.1 | 1.4±0.1 |

The autocorrelation function of the q factor for the DMC \(C_C\) also shows a ~4 ps oscillation, which is better observed in the residuals of its bi-exponential fitting (Figure 4.5) and is not observed in its cyclic analogue. The oscillation in the autocorrelation reveals a periodic motion that affects the tetrahedral structure of the coordinated carbons in this timescale. Due to the simplicity of the studied system, it is fair to assume that the oscillation is caused by the close proximity between the cation and the anion in DMC due to the formation of SSIPs. To test this hypothesis, the autocorrelation function of the distance between Li+ and the phosphorus atom of the anion was calculated. As in the q factor, an oscillation with a period of 7 ps is observed in the autocorrelation of the DMC system, but not in BC. Note that the factor of two between the oscillation periods observed in the autocorrelation of the q factor and the Li-anion distance arises from the definition of q (Figure 4.6). To simplify the process, assuming the PF6- only pushing the
two nearby carbons in a scissoring-like motion, the evolution of $q$ along the change of C-O-C angle is shown in Figure 4.6. One period of lithium oscillation, which is inserting in and then getting out of the solvation shell, is in corresponding to the angle change from 40 to -40, then from -40 back to 40. From Figure 4.6, $q$ experiences two cycles within one cycle of Li-PF6 distance change, which explains the factor of 2 between the oscillation periods. Thus, the oscillation in the $q$ autocorrelation indicates that the anion disturbs the tetrahedral structure by pushing the nearby carbonyl groups back and forth while alternating between two different structures related to SSIPs (see Figure 4.12).

![Figure 4.5. The residuals of the bi-exponential fitting of the ACF of $q_C$ of DMC.](image)
Figure 4.6. Variation of $q$ during the insertion of a PF$_6^-$ anion in the Li(DMC)$_4^+$. 

Figure 4.7. Distributions and autocorrelation functions of the Li-O-C$_C$ (top panel), and C$_C$-Li-C$_C$ (bottom panel) for BC (black solid line) and DMC (red dashed line) samples.
An examination of the different geometrical parameters, such as Li-O<sub>c</sub> distance and O<sub>c</sub>-Li-O<sub>c</sub> angles confirms the results derived from the q factor, in which the Li-O<sub>c</sub>-C<sub>c</sub> geometrical factor exhibits the largest difference between samples for their distributions and dynamics (see Table 4.1, and Figure 4.8 for the Li-O<sub>c</sub> distance and Figure 4.9 for O<sub>c</sub>-Li-O<sub>c</sub> angle). While BC and DMC Li-O<sub>c</sub>-C<sub>c</sub> angle distributions depart significantly from the 180° expected for a perfect tetrahedral structure (Table 4.1), the DMC solvation shell presents a much broader and asymmetric distribution for the Li-O<sub>c</sub>-C<sub>c</sub> angle than BC. This result indicates that the DMC carbonyl carbons undergo larger spatial fluctuations than BC, which are related to the formation of SSIPs (see next section). The dynamics of the Li-O<sub>c</sub>-C<sub>c</sub> autocorrelation function reveals two dynamical processes in which the slow has a characteristic time of ~3 ps and ~5 ps for DMC and BC, respectively. The difference in Li-O<sub>c</sub>-C<sub>c</sub> bending dynamics evidences the slower carbonyl motions of the BC-Li+ solvation shell, due to intercalation which is not present in the DMC solvation shell.

Figure 4.8. Distributions (left) and autocorrelation functions of the distance between Li and O<sub>c</sub> in BC (black, solid) and in DMC (red, dash).
Figure 4.9. Distributions (left) and autocorrelation functions of O\textsubscript{C}-Li-O\textsubscript{C} angle in BC (black, solid) and in DMC (red, dash).

A more evident distortion of the BC solvation shell is observed by studying the C\textsubscript{C}-Li-C\textsubscript{C} angle. The mean values (standard deviations) of C\textsubscript{C}-Li-C\textsubscript{C} angle are 104.8 (30.4) and 108.4 (17.9) for BC and DMC solvation shells, respectively. The result shows that BC has a more tilted geometry than DMC when coordinated to Li+. Interestingly, the C\textsubscript{C}-Li-C\textsubscript{C} angle has a much broader distribution for BC than DMC. The difference in the distributions arises from the intercalation of the second solvation shell, which forces the carbonyl carbons to depart from the tetrahedral structure. The characteristic times of ~22 ps for BC and ~6 ps of DMC derived from the autocorrelation function of the C\textsubscript{C}-Li-C\textsubscript{C} angle also shows the striking differences between BC and DMC solvation shells. The slow dynamics is compatible with the intercalation observed in the BC samples since the compact BC solvation shell requires the displacement of one intercalated BC molecule to produce large motions of the BC molecules in the Li+ solvation shell.

The results showed so far demonstrate that the solvent molecules beyond the first solvation shell play a role in the solvation of the lithium by either inserting the groups or by intercalating themselves in the first solvation shell. However, unlike the solvent molecules in the first solvation
shell of Li+, the solvent molecules in the second solvation shell undergo larger changes in its position due to the lack of a strong interaction with Li+. The fast dynamics of the molecules in the second solvation shell is directly observed in the time evolution of their orientational dynamics which are 10 and 4 times faster than those in the first solvation shell for DMC and BC samples, respectively (Figure 4.10). The orientational autocorrelation time of carbonate molecules was estimated by averaging the scalar product of the normalized dipole \( \tilde{\mu}_i \) of each carbonate molecule (i) in the system as

\[
C_1(t) = \langle \tilde{\mu}_i(t)\tilde{\mu}_i(0) \rangle = \frac{1}{N} \sum_{i=1}^{N} \cos(\theta_i(t))
\]

where \( \theta_i(t) \) is the angle between the dipole of the molecule at 0 time and time \( t \). The results are shown in Figure 4.10, and the decorrelation times derived from the fittings of the values in Figure 4.10 with a function of the form:

\[
f(t) = \sum a_i \exp(- t / \tau_i)
\]

are presented in Table 4.2.
Figure 4.10. Orientational autocorrelation of the different solvation shells of Li+ for DMC (left panel) and BC (right panel) samples. The black and red lines correspond to the first and second solvation shell of Li+, respectively.

Table 4.2 Fitting parameters for orientational autocorrelation of the different solvation shells of Li+ for DMC and BC samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a_1$ (ps)</th>
<th>$\tau_1$ (ps)</th>
<th>$a_2$</th>
<th>$\tau_2$ (ps)</th>
<th>$a_3$</th>
<th>$\tau_3$ (ps)</th>
<th>$&lt;\tau&gt;$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC 1$^{st}$ SS</td>
<td>0.04±0.01</td>
<td>0.2±0.1</td>
<td>0.13±0.01</td>
<td>3.6±0.5</td>
<td>0.83±0.01</td>
<td>91±7</td>
<td>76±6</td>
</tr>
<tr>
<td>BC 2$^{nd}$ SS</td>
<td>0.13±0.01</td>
<td>0.8±0.1</td>
<td>0.86±0.01</td>
<td>22.6±0.1</td>
<td>--</td>
<td>--</td>
<td>19.7±0.1</td>
</tr>
<tr>
<td>DMC 1$^{st}$ SS</td>
<td>0.21±0.01</td>
<td>2.8±0.3</td>
<td>0.75±0.01</td>
<td>48±2</td>
<td>--</td>
<td>--</td>
<td>38±2</td>
</tr>
<tr>
<td>DMC 2$^{nd}$ SS</td>
<td>0.62±0.01</td>
<td>1.5±0.1</td>
<td>0.38±0.01</td>
<td>8.1±0.5</td>
<td>--</td>
<td>--</td>
<td>4.0±0.3</td>
</tr>
</tbody>
</table>

Overall, the presented results show that the dynamics of the first solvation shell of Li+ is controlled by both the second solvation shell and the anion. In the case of DMC, the motions of the solvation shell are essentially two, one which is exclusively driven by the motion PF$_6^-$ ion and another given by stochastic fluctuations in system. In contrast, the Li+ solvation shell of BC only present a motion related to thermal fluctuations because of the intercalation of BC molecules into the first solvation shell, which hinders the formation of SSIPs and consequently its influence in the dynamics of the Li+ solvation shell deformation.
4.3.2. Anion solvation

The structure of the solvation shell of hexafluorophosphate anion was also investigated. The RDF between lithium and the phosphorus atom for BC and DMC samples are displayed in 4.11. The RDFs show significant differences between the two systems. First, the first peak of the DMC RDF is wider and more asymmetric than that of BC. Second, the location of the peak maxima is also different: 6.1 Å for DMC and at 8.2 Å for BC. The peak maxima demonstrate that the interaction between lithium and the anion is inhibited by the presence of BC molecules, but not by linear carbonates. According to the RDF of the Li-Oc, the second solvation shell ends at ~7.5 Å. Consequently, the anion positions at 8 Å and 6 Å are assigned to free ion and solvent separated ion pairs, respectively. Note that this assignment is similar to that previously derived from IR experiments.[20] Thus, the dominant species for the anion are free ions in BC and SSIPs in DMC. Although DMC shows predominantly SSIPs, the RDF of Li-P presents a shoulder at 7.0 Å. This latter peak corresponds to free ions in DMC. However, some of the free ions are not completely “free” since they present a CH₃--F interaction that stabilizes their structure similar to an SSIP (Figure 4.11). In addition, the shoulder at ~6 Å in the BC RDF demonstrates that the anion has a small probability of forming SSIPs in BC.
Figure 4.11. RDF between lithium ion and the phosphorus atom of PF$_6^-$ ion for BC (black solid line) and DMC (red dashed lines) samples.

The RDF shows that the anion is present in both free and SSIP in DMC, but mainly as free ions in BC. The lack of SSIPs in the cyclic carbonate and the observation of SSIPs and free ions in the linear carbonate is in agreement with previous experimental studies.[21] The molecular mechanism for the inhibition of the SSIP formation in cyclic carbonates could arise from a difference in the energetics of the SSIP formation. However, previous studies have shown that linear and cyclic carbonates have similar ion pair energetics when only accounting for 4 carbonates in the solvation shell.[31] However, the RDF of the carbonates indicates that BC has ~7 carbonates in the first solvation shell due to the intercalation. The presence of 7 BC molecules creates a denser solvation shell around Li$^+$ which not only limits the interaction between the cation and the anion, but also requires the expulsion of more than one BC molecule to create CIPs. In addition, the intercalated BC molecules appear to have their dipole moment pointing away from Li$^+$, making it energetically unfavorable to position the counter ion closer to Li$^+$ due to the repulsive ion-dipole interaction. Finally, the RDFs of both systems do not show anions at distances less than 4 Å from Li$^+$. The result indicates that contact ion pairs are not the most favorable counterion species in dilute solutions, irrespective of the carbonate structure.
Due to the limited time window explored by the canonical AIMD simulation, the probability of forming different anionic species was studied by computing the potential of mean force (PMF) from AIUS simulations. Figure 4.13 shows the calculated PMF for a Li-P reaction coordinate. Both carbonate samples exhibit a potential well with a minimum centered at ~3 Å, which is related to the formation of CIPs. An extra potential minimum is observed at ~3.6 Å in Li-P PMFs for DMC, which is less noticeable in BC. This minima at ~3.6 Å is assigned to a SSIP; i.e., four carbonate molecules and the anion in the Li+ solvation shell (Figure 4.12). Overall, the energy barriers of ~1.5 kcal/mol are observed in DMC and BC systems, which are well within thermal energy. Moreover, the energy difference between CIP, SSIPs and free ions is also within ~1 kcal/mol indicating that the ion pair formation does not impart a large energy stabilization of the system.

The normalized probability of finding the phosphorus atoms of the anion at distance r of Li+ computed from the Boltzmann distribution function is shown in Figure 4.13. While it appears that CIP have a large probability because of the radial distribution, the space integrated probability (Figure 4.13) shows that the CIP only account for ~14% in DMC and ~12% in BC. However, the
most significant difference in the integrated probability is the formation of SSIPs in DMC. For the cutoff of range of 3.4-6.4 Å (Figure 4.11), the SSIP population accounts for 46% and 40% in DMC and BC, respectively, and the free ion population is 40% in DMC and 48% in BC. These results, along with the RDF of Li-P from the canonical AIMD, support the previous experimental data that the lithium ion exists predominantly as SSIP in DMC, while in BC it exists predominantly as free.[20] Note that the semi-qualitative agreement between experiment and theory could arise from the relatively small time window sampled in our AIUS because of the high computational cost of the methodology.

Figure 4.13. Ion pairing in BC and DMC. PMF of ion pairing process (top panel), probability distribution of PF$_6^-$ existing at the distance of r of lithium ion (middle panel), and integrated probability of PF$_6^-$ existing in a sphere with a radius of r (bottom panel) for BC (black solid line) and DMC (red dashed lines) samples.
4.3.3. Solvent exchange

The canonical AIMD trajectory revealed that solvent exchange is a slow dynamical process since there is only one occurrence in the 200 ps trajectory of the BC-Li+ system and it is not observed in the DMC trajectory. Thus, the canonical AIMD strongly suggests a slow solvent exchange rate, which is in agreement with a previous theoretical study.[2] However, the observed slow dynamics also prevents us from estimating the rate constant value because of the large statistical error. To estimate the chemical exchange rate, the structural arrangement of the solvation coordinate in BC giving rise to the only solvent exchange event observed in the BC trajectory is used. This structural arrangement is likely to represent the geometry of transition state (TS).

![Figure 4.14. Kinetic scheme for chemical exchange including the transition state (TS) geometry observed in the BC trajectory.](image)

The observed transition state (Figure 4.14) shows that the carbonate molecules adopt a trigonal bipyramid in which the incoming carbonate approximates to the Li+ through an axial position. While this solvent configuration (i.e., bipyramidal geometry of the carbonates) does not appear frequently in the trajectory, the solvent configuration showing five carbonates in the Li+ solvation shell does. Therefore, one can use the appearance of the TS during the canonical trajectory to obtain the lower limit of the time scale for the solvent exchange dynamics. To this end, it is assumed that the complex containing 5 carbonate molecules and one Li+ undergoes chemical exchange as depicted by the following mechanism.
\[
\begin{align*}
\text{BC} + C_4 & \rightleftharpoons \text{C}_5(TS) \rightleftharpoons C_4' + BC', \\
& \quad \text{where } C_4' \text{ and } C_4 \text{ are the Li+ with four carbonates in its first solvation shell, } C_5 \text{ is the five-carbonates configuration, and } BC' \text{ is the carbonate interchanged during the solvent exchange process. In addition, } k_i \text{ are the rate constants of the depicted kinetics steps. Since the concentration of BC does not change in the solution during the process, the equation can be simplified as,}
\end{align*}
\]

\[
\text{C}_4 \rightleftharpoons \text{C}_5(TS) \rightleftharpoons C_4'.
\]

In this case, the concentration evolution can be solved as:

\[
\begin{align*}
[C_5(t)] &= A_0k_1 \left[ \frac{k_{-2} - \gamma_1}{\gamma_1(\gamma_2 - \gamma_1)} e^{-\gamma_1 t} + \frac{k_{-2} - \gamma_2}{\gamma_2(\gamma_2 - \gamma_1)} e^{-\gamma_2 t} \right], \\
[C_4'(t)] &= A_0k_1k_2 \left[ \frac{1}{\gamma_1\gamma_2} - \frac{1}{\gamma_1(\gamma_2 - \gamma_1)} e^{-\gamma_1 t} + \frac{1}{\gamma_2(\gamma_2 - \gamma_1)} e^{-\gamma_2 t} \right],
\end{align*}
\]

where \( \gamma_1\gamma_2 = k_{-1}k_{-2} + k_1k_2 + k_1k_{-1} \); \( \gamma_1 + \gamma_2 = k_1 + k_{-1} + k_2 + k_{-2} \), with the boundary condition of \( [C_4(0)] = A_0 \quad [C_5(0)] = 0 \), and \( [C_4'(0)] = 0 \). In addition, the final state and the initial state are actually identical, and so: \( k_1 = k_{-2} \), \( k_2 = k_{-1} \), and \( k_1 \ll k_{-1} \).

Thus,

\[
\begin{align*}
[C_5(t)] &= A_0k_1 \left[ \frac{1}{2k_{-1}} - \frac{1}{k_1 + 2k_{-1}} e^{-(k_1 + 2k_{-1})t} \right], \\
[C_4'(t)] &= 0.5A_0(1 - e^{-k_1 t}).
\end{align*}
\]
From this mechanism, one can demonstrate that the solvent exchange rate is given by the rate of making the transition state; i.e., $k_1$.

The rate of making the $C_5$ was obtained from the time intervals between the appearances of the $C_5$ from the AIMD trajectory. In this case, the $C_5$ was strictly defined as the Li$^+$ coordinated with five carbonates in which all carbonates have the carbonyl carbon within 3.5 Å of the Li$^+$. The time intervals between the appearances of two different $C_5$ configurations are displayed in 4.15. The time intervals show that the BC solvation shell is more likely to adopt the $C_5$ configuration than DMC. In addition, it is observed the presence of time intervals with time windows of 0.5 ps. These short time intervals correspond to the oscillation in the structure that do not completely lose the $C_5$ configuration. In contrast, the longtime intervals observed in the trajectory relate to the time required to form the five carbonate structure. The average time for forming $C_5$ configuration in BC and in DMC are found to be 27 ps and 60 ps, respectively. Based on the results calculated from the time intervals, the rate of chemical exchange (or equivalent $1/k_1$) is estimated to be $(27 \text{ ps})^{-1}$ for BC and $(60 \text{ ps})^{-1}$ for DMC. Overall, the solvent exchange dynamics in DMC-Li$^+$ system is much slower than that of BC-Li$^+$ complex. It is likely that the intercalation of the second solvation shell in BC might help to rearrange the molecules in the first solvation shell in a geometry close to that of the TS. In contrast, the less extended solvation shell formed by the DMC limits the insertion of the fifth carbonyl group required for the solvent exchange process to occur.
The predicted solvation exchange process is much slower than the 5 ps proposed experimentally and theoretically.\cite{18, 19} However, it is possible that the short time window of the canonical trajectory is not sufficient to appropriately sample the solvent exchange process. To this end, AIUS was performed in both DMC and BC systems. The PMFs of the solvent exchange for BC and DMC are shown in Figure 4.15. Surprisingly, the solvent exchange process for BC and DMC show a similar energy barrier of ~1 kcal/mol. To estimate the solvent exchange rate from the PMF, Kramer’s theory is used. In Kramer’s theory, the rate constant of a transition state is given by
\[ k = \frac{\omega_0 \omega_b}{2\pi \gamma} e^{-\frac{E^*}{k_BT}}, \]

where \( E^* \) is the transition state energy barrier, \( \gamma \) is the friction coefficient, and \( \omega_0 \) and \( \omega_b \) are the oscillation frequencies at the bottom of the well and at the transition state, respectively. In this case, the solvent exchange rate is computed for the breaking process, since the forming process requires the oscillation frequency of the final state, which is not available due to the limit of the box size. However, the PMF shows that the potential well of the final state for making a bond is much flatter than that of the initial state, indicating that the making process should be slower than the breaking process. Using the oscillation frequencies, \( \omega_0 \) and \( \omega_b \), obtained by assuming the harmonic potential, the characteristic time of breaking is found to be on a range of 100-370 ps for BC, and of 20-60 ps for DMC. Although the energy barrier of \(~1 \text{ kcal/mol}\) does not fulfill the one of the hypothesis of Kramer’s theory, the observed characteristic time is similar to that predicted from the kinetics of the TS in canonical simulations. Thus, the solvent exchange rates derived from the rate of making and breaking the TS and Kramer's theory confirm that the rates are much longer than the ones previously derived from experiment.[18]

4.4. Conclusions

The *ab initio* molecular simulations presented here show the similarities and differences in the structure and dynamics of the lithium solvation shell in cyclic and linear carbonates. A tetrahedral coordination number was found for the lithium ion in both DMC and BC solutions. In addition, it is observed that the methyl groups of various DMC molecules insert into the lithium ion first solvation shell. In contrast, three BC molecules intercalate in the first solvation shell of the lithium ion for this cyclic carbonate. The intercalation of BC molecules leads to a more rigid
and more organized solvation shell in BC than DMC. The speciation of Li+ is also affected by the chemical nature of the carbonate, where the intercalation of BC molecules appears to inhibit the association of Li+ with the counterion in BC. The PMF derived from AIUS shows that Li+ exists predominantly as free in BC and SSIPs in DMC, and that CIPs only account for a small fraction of the total population (~10%). In addition, the canonical AIMD and AIUS via Kramer’s theory predict a slow solvent exchange dynamic in both DMC and BC with characteristic times ranging from fifty to hundreds of picoseconds. Overall, this work gives a description of the structure and dynamics of the lithium solvation shell in cyclic and in linear carbonates occurring in picosecond time scales. In addition, it demonstrates that the carbonate molecular structure affects the speciation of Li+ and solvent exchange dynamics.

4.5. References


134


CHAPTER 5
MOLECULAR STRUCTURE OF A CONDUCTIVE AND “NON-IONIC”
MIXTURE OF MOLECULAR SOLVENTS

5.1. Introduction

Proton delocalization plays a critical role in the structure and function of both aqueous solution and biological macromolecules. In the system of excess aqueous proton and water, strong evidence for proton delocalization with a low-barrier, double-minimum potential energy surface (PES) in Zundel-like cation motif was found by 2DIR and pump-probe spectroscopies.[1, 2] It implies a possible mechanism of proton transport in water that is responsible for the high conductivity of the excess proton water system. In terms of macromolecules, the role of low-barrier hydrogen bond (LBHB) in catalysis processes, which is an abnormally short hydrogen bond with a proton transfer barrier of the same order as zero-point energy, has been discussed for a long time. Unusually high prevalence of LBHB was found in the enzymes with transition state analog, and many scientists insist that the low-barrier hydrogen bond contributes to enzymic catalysis by stabilizing its transition state energy through quantum resonance.[3-9] Meanwhile, the delocalization of excess protons along the conducting wire was also found in the membrane enzymes, and the fluctuation of soliton in the molecule chain under the condition of strong coupling is the mechanism of proton transfer in the conducting channel.[10-13] Similarly, the delocalization of excess proton through the Grotthuss hopping mechanism in the hydrophilic domain pocket was found to be the reason for the high proton mobility in proton-conducting membranes as Nafion.[14] Other applications of proton delocalization appear as manipulating the isotopic fractionation factor by utilizing the low barrier potential and the different zero-point energy of isotopes.[15]
Attractions have been drawn to a system composed of acetic acid (HAc) and N-methylimidazole (C$_1$Im). A Brønsted acid-base mixture of weak acid HAc and weak base C$_1$Im with an extremely low ionicity was found to have a conductivity 4 orders of magnitude higher than its neat acid and 2 orders of magnitude higher conductivity than its neat base. This high conductivity is unexpected since the conductivity of the acid-base mixture is believed to be related to the ∆pKa between the two components, which indicates the concentration of ions. Raman spectroscopy showed that electrically neutral molecular species predominantly exist in the equimolar mixture,[16] in which the conductivity of 4 mS/cm was found.[17] Moreover, measurements of different molar ratios of this HAc/C$_1$Im mixture have been conducted to obtain the conductivity curve, and then two electrical conductivity maxima were found in the curve, at xHAc=0.65 and xHAc=0.85 respectively.[18, 19] This double-maxima is unique compared with other conductive acid/base mixtures such as pyridine/acetic acid, trimethylamine/acetic acid, water/acetic acid, etc.,[18] indicating a specific mechanism of electric conductivity.

Efforts were made to explain the unique proton activities and electric conductivity in this system. By looking into the Waldon plot, and conducting simple DFT energy calculations, Umebayashi and co-workers claimed that the system is a good or superionic liquid with a specific conductive mechanism such as the Grotthuss mechanism. ∆pKa value, which is pKa(C$_1$HIm$^+$) - pKa(HAc), is as small as 2.4 in this system, precluding the complete proton transfer. On the other hand, they claimed that the energy difference between the molecule complexes and ion pairs is approximately 7 kJ/mol, which is comparable to the thermal energy. This small energy difference enables fast proton transfer followed by the reorientation of surrounding neutral molecules, implying a specific proton conduction.[16] Moreover, recent ab initio molecular dynamics simulation provided evidence of the Grotthuss mechanism in the equimolar mixture, herein the
content of neutral species is 75-80%.[20] The energy surface of the proton transfer after zero-point energy correction showed a barrierless profile with a 7 kJ/mol energy difference between the two configurations.[20] However, nuclear magnetic resonance (NMR) experiments demonstrated completely different results. Enthalpy change of -9.33 kJ/mol, and entropy change of 11.29 J·(mol·K)⁻¹ in proton transfer process were calculated by temperature-dependent NMR, along with an ionicity of 92.8% obtained from concentration-dependent NMR.[21] This work was based on the simple assumption that the proton exists either in single HAc molecule or in a single C₁HIm⁺ ion.

This barrierless energy profile indicates a probability that the proton delocalization exists in the HAc/C₁Im mixture. In the past thirty years, there have been numerous experimental and theoretical studies uncovering proton delocalization in low-barrier or barrierless potential for both homonuclear and heteronuclear hydrogen bonds. In the case of the weak homonuclear hydrogen bond, formation energy is small (~20 kJ/mol) and the distance between two electronegative atoms is far (>2.8 Å for O-O). The hydrogen is in a double-well potential, attached to either one electronegative atom closely by a covalent bond and far away from the other. As two electronegative atoms get closer, the barrier between two potential wells decreases and eventually can be overcome by the zero-point energy.[22] In this case, the shared proton is described to move freely between the two electronegative atoms and be bonded covalently to them.[23] An even closer distance between two atoms results in a single-well potential.[22] Similar trend has also been observed for heteronuclear hydrogen bonds.[22]

In this project, we looked into the structures and dynamics in the HAc/C₁Im mixture by FTIR, NMR, and DFT computational technique. The existence of proton delocalization in different structures is then discussed.
5.2. Experimental and theoretical methods

5.2.1. Sample preparation

1-methylimidazole (99% pure, Alfa Aesar) was dried over molecular sieves 4A for several days, and acetic acid glacial from VWR was dried by desiccant-anhydrous drierite (10-20 mesh no indicate) from W.A. Hammond Drierite Company, Ltd. for more than three days.[16] Mixtures were prepared at C$_1$Im to HAc molar ratio of 100:1, 20:1, 10:1, 2:1, 1:1, 1:2, and 1:5. The drying process and sample preparation process were all performed in a nitrogen-filled glovebox, and the final mixtures were checked by the Karl Fisher titration to ensure a water content less than 100 ppm.

5.2.2. Linear infrared spectroscopy

Fourier transformed infrared spectroscopy (FTIR) were collected on a Bruker Tensor 27 equipped with a liquid nitrogen cooled narrow band MCT detector, with a resolution of 0.5 cm$^{-1}$. Sample cells for FTIR were prepared by sandwiching samples two CaF$_2$ windows and operated in the N$_2$-filled glovebox. Attenuated total reflection (ATR) – FTIR were run on a Bruker Tensor 27 spectrometer equipped a room temperature DTGS detector, mid-IR source (4000 to 400 cm$^{-1}$), and a KBr beamsplitter. The maximum resolution is 1 cm$^{-1}$. The standard sample cell, which is a Pike Miracle single-bounce attenuated total reflectance (ATR) cell equipped with a ZnSe single crystal, was used for measurements. All ATR data were collected as an average over 16 scans at a resolution of 4 cm$^{-1}$.

5.2.3. Conductivity and viscosity measurements

Electrical conductivity was measured with a conductivity meter (YSI 3200 conductivity instrument). Viscosity was measured with a viscometer (Brookfield, DV-II+ Pro).
5.2.4. **Density functional theory (DFT) calculations**

DFT calculations of optimization and frequency calculation in vacuum were performed by Gaussian 16 software at PBE level with 6-311++G basis set.[24] Initial configurations were built by Avogadro[25] with classical force field MMFF94, and were firstly optimized using a 6-311G basis set. To investigate the potential well, distance scan of O-H was performed. Optimization energy at MP2 level with 6-311++G was also calculated for comparison.

5.2.5. **Ab initial molecular dynamics simulation (AIMD)**

AIMD simulations were carried out by using CP2K package (version 5.1).[26] The electronic structure was calculated via Quickstep module[26] using the PBE functional with the D2 dispersion scheme[27] and the TZV2P basis set, with Goedecker-Teler-Hutter (GTH) pseudopotentials.[28-30] Periodic boundary conditions were applied to all the systems, and the Nosé-Hoover thermostat was used to keep the temperature as a constant of 300 K with the temperature damping constant of 100 fs. A self-consistent field (SCF) convergence criterion was set to $5.0 \times 10^{-7}$ Hartree. The four systems with different molar fractions of HAc were performed by four boxes, with 72 HAc molecules for pure acetic acid (system 1), 60 HAc and 10 C$_1$Im for $x$(HAc)=0.85 (system 2), 42 HAc and 21 C$_1$Im for $x$(HAc)=0.67 (system 3), and 1 HAc and 51 C$_1$Im for very diluted solution (system 4). Cubic boxes with box size of ~19 Å were applied for all the systems. System 2 and 3 are representative of the mixture at its two conductivity maximums.[18, 19]

Boxes were prepared by Packmol,[31] and Optimized Potential for Liquid Simulations-all atom (OPLS-aa) forced field[32] was applied. The system first underwent an energy minimization, a 10 ns NVT, a 10 ns NPT, and a 10 ns NVT process using Large-scale Atomic/Molecular
Massively Parallel Simulator (LAMMPS) software package[33] and OPLS-aa force field. Initial configurations for AIMD simulation were obtained by taking three random snapshots separated by more than 200 ps from the second NVT process of the classical MD simulation to assure equilibrium and better sampling. In the AIMD, each system has 3 trajectories, each with different initial configuration. The systems were equilibrated for ~4 ps, followed by a 100 ps productive run for system 2 and 3, and a 35 ps productive run for system 1 and 4. In all cases, the time step of AIMD simulation is 0.5 fs.

5.3. Results

Conductivity measurement results of HAc/C\textsubscript{1}Im mixture at different HAc molar fractions are plotted in Figure 5.1. In agreement with previous studies, two maximums occur at around 65% and 85%, with the conductivity several orders higher than pure HAc or C\textsubscript{1}Im. [18, 19] Conductivity increases slowly and linearly in the range of 0 < x(HAc) < 0.4, and experiences fast increase after x(HAc) > 0.4, indicating an obvious change of dominant hydrogen bond network structure at x(HAc)=~0.4. In the x(HAc) range of 0.4 - 0.9, two maximums emerge with an obvious drop in between at 0.75. At x(HAc) > 0.9, solution conductivity experiences a fast linear decreasing.

There are two types of conduction mechanisms in the solution. One is the “vehicle” mechanism, where the charge transfers with the diffusion of carrier ions, determined by ionicity and viscosity; the other is the Grotthuss-like mechanism, where the charge is transported through the hydrogen-bond network by bond shifting without large translations of the proton. The conductivity of sodium acetate and acetic acid mixture at the molar fraction of x(NaAc) = 0.04 was measured at room temperature, and it is 0.26 mS/cm. According to the previous study, in HAc/pyridine mixture, the degree of ionization reaches 0.04 at x(HAc) = 0.7.[34] Consider the similar pKa of pyridine and C\textsubscript{1}Im, the degree of ionization of two should not deviate too much. In
this case, if the “vehicle” mechanism is dominant in the HAc/C$_1$Im mixture, the conductivity of HAc/C$_1$Im at $x$(HAc)=0.7 should be at the same scale as the conductivity of HAc/NaAc at $x$(NaAc)=0.04, since they have the same ion concentration. Considering the high viscosity of HAc/C$_1$Im, HAc/NaAc mixture is supposed to have even higher conductivity than the HAc/C$_1$Im mixture at the same degree of ionicity. However, in reality, the HAc/NaAc mixture has a much lower conductivity (0.26 mS/cm) compared to the HAc/C$_1$Im mixture (7.9 mS/cm), ruling out the “vehicle” mechanism.

Comparing the conductivity curve with the viscosity curve measured for the mixture in Figure 5.1, it can be seen that the maximum of viscosity occurs at the same concentration range of the maximum conductivity, which implies that the conductivity is not mainly dependent on the diffusion of ions in the solution. This result is in agreement with the possible Grotthuss proton conduction mechanism proposed by several groups previously.[20, 35] Viscosity at the concentration of the maximum conductivity is around 10 times higher than that of the pure acetic acid or methyl imidazole, indicating a highly ordered structure with stronger interaction among molecules at this concentration. Walden product shown in Table 5.1 provides a single maximum at $x$(HAc)=0.75. This demonstrates that the concentration of charge carrier, which is proton in this case, reaches its maximum at $x$(HAc)=0.75. However, the high viscosity at the same molar fraction decreases the conductivity, resulting in a local minimum, and two maximums at each side of $x$(HAc)=0.75.
Figure 5.1. Conductivity and viscosity of HAc and C$_1$Im mixture at different molar ratio

Table 5.1. Walden product of HAc and C$_1$Im mixture at different molar ratio

<table>
<thead>
<tr>
<th>x(HAc)</th>
<th>conductivity (mS/cm)</th>
<th>viscosity (cP)</th>
<th>Walden product</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>8.0</td>
<td>11.4</td>
<td>91.2</td>
</tr>
<tr>
<td>0.70</td>
<td>7.9</td>
<td>16.4</td>
<td>129.56</td>
</tr>
<tr>
<td>0.75</td>
<td>7.9</td>
<td>18.3</td>
<td>144.57</td>
</tr>
<tr>
<td>0.80</td>
<td>6.4</td>
<td>16.9</td>
<td>108.31</td>
</tr>
<tr>
<td>0.85</td>
<td>8.0</td>
<td>12.6</td>
<td>101.14</td>
</tr>
</tbody>
</table>

The ATR-FTIR spectra of HAc/C$_1$Im mixture at different molar ratios in the frequency range of 1600-3800 cm$^{-1}$ are shown in Figure 5.2. The sharp peak centered at ~1700 cm$^{-1}$ is the absorption of COO asymmetric stretching mode in HAc,[36] which is in agreement with the decrease of the peak height as the decrease of HAc concentration. At very low molar fraction of HAc, there only exists absorption of the H motion in C$_1$Im at ~2900 cm$^{-1}$ and 3100 cm$^{-1}$. As the HAc concentration increases, three broadband peaks, located at ~1900 cm$^{-1}$, 2500 cm$^{-1}$, and 3000 cm$^{-1}$ respectively, increase and then decrease. The 1900 and 2500 cm$^{-1}$ peaks reach maximum at the molar ratio HAc to C$_1$Im 2:1 (x(HAc)=67%), while the 3000 cm$^{-1}$ peak reaches its maximum at x(HAc)=83%, indicating two different dominant structures in the different mixtures. Although it is on top of the pure acetic acid CH$_3$ peak as shown at the bottom of Figure 5.2, the peak at 3000 cm$^{-1}$ arising from the mixture is still clear. All three peaks have an extremely large bandwidth of around 1000 cm$^{-1}$, which is similar to the broadband IR absorption observed for the excess proton.
motions in water. To look into the absorption at low HAc concentration with better signal to noise ratio, FTIR spectra were measured with thicker spacers, and are shown in Figure 5.3 after the subtraction of the C\textsubscript{1}Im background. The noises in the range of 2900 cm\textsuperscript{-1} to 3150 cm\textsuperscript{-1} result from the subtraction of over absorption in the C\textsubscript{1}Im range. It is interesting that although the broadband peaks grow with the increasing concentration of HAc, the ratio of peaks at 1900 and 2500 cm\textsuperscript{-1} keeps as constant. This indicates that in much diluted HAc mixtures, there exist two main structures, and the area ratio of these two does not vary with HAc concentration.

![Figure 5.2. ATR-FTIR spectra of HAc and C\textsubscript{1}Im mixture at different molar ratio.](image)

Figure 5.3. FTIR spectra of HAc and C1Im mixture at small x(HAc).

5.4. Discussions

5.4.1. Assignment of infrared peaks

Previous studies on delocalized excess protons in water have built a relationship between broadband FTIR peaks and motions of excess protons. Although the assignment of Eigen and Zundel species of proton is still under debate, the broadband peak centered at 1200 cm\(^{-1}\) is mostly assigned as the stretching motion of the strongly bound proton in Zundel arrangement, [2, 37-40] 1750 cm\(^{-1}\) peak is attributed to bending motions of aqueous proton complex,[38, 39, 41-45] and the peaks at 2500 cm\(^{-1}\) and 3000 cm\(^{-1}\) are assigned to flanking water OH stretches in different aqueous proton water cluster configurations.[1, 37, 38, 41-44, 46-48] To this end, DFT frequency calculation was implemented to investigate the corresponding motion of IR absorption in this HAc/C1Im system.

To simulate the system near the maximum conductivity area, based on our AIMD simulation, previous Raman and \textit{ab initio} molecular dynamics studies,[16, 20] acetic acid chains of length L=1-5 with C1Im as their terminate were interrogated. Chains with L>5 were not calculated because from previous study and our own MD simulation, the proportion of L>5 chains
in all the mixtures is negligible. As shown in Figure 5.4, there exist two kinds of structure arrangement, each with an energy local minimum. DFT frequency computational results of planar Figure 5.4(a) structures are shown in Figure 5.5(a), and the results of Figure 5.4(b) are shown in Figure 5.5(b).

![Figure 5.4. Two arrangements of HAc and C1Im complex](image)

In the frequency range of 1500 ~1750 cm\(^{-1}\), absorptions with small infrared intensity less than 1000 km/mol are generated from the coupling between the COO stretching and proton bending. Single proton stretching motion displays a high infrared intensity of around 2000 – 3000 km/mol, standing out from other motions in this frequency range, which have intensities on the scales of tens and hundreds. Hydrogen bond proton in the HAc molecule adjacent to C1Im is denoted as the 1\(^{st}\) proton, and the other protons in the complex are denoted as 2\(^{nd}\), 3\(^{rd}\), 4\(^{th}\), and 5\(^{th}\) protons from C1Im side to the other. The stretching motion of the 1\(^{st}\) proton has an extremely strong absorption at ~2500 cm\(^{-1}\) in both two structures at L=1. At L>1, infrared absorption of this stretching locates at frequency of around 1800 cm\(^{-1}\) with highest intensity at L=2. The stretching frequency of 2\(^{nd}\) proton locates at ~3000 cm\(^{-1}\) in structure (a) at L<4 and structure (b), which in structure (a) at L>3 it locates at ~2300 cm\(^{-1}\). The rest proton stretch modes locate at ~3000 cm\(^{-1}\) with intensity of around 1000 km/mol. Based on the calculation, the 1900 cm\(^{-1}\), 2500 cm\(^{-1}\), and 3000 cm\(^{-1}\) peaks in infrared spectra at x(HAc) > 0.1 can be assigned to stretching of the 1\(^{st}\) proton at L>1, 1\(^{st}\) proton at L=1, 2\(^{nd}\) proton at L>3, and the rest protons respectively. This assignment agrees with the fact that the 1900 cm\(^{-1}\) peak reaches its maximum at x(HAc) =0.65 and decreases to 0 at x(HAc)=1, while the 2500 cm\(^{-1}\) and 3000 cm\(^{-1}\) peaks keep increasing until reaching its
maximum at \(x(\text{HAc})=0.85\). The reason for this is that at lower HAc concentration, increasing of HAc molar fraction leads to the increasing of concentration of L=1 and L=2 structures, while at higher concentration, chain length increasing becomes a competing effect and causes the 1900 cm\(^{-1}\) absorption to decrease.

![Figure 5.5. DFT frequency calculation of planar linear HAc/C\(_1\)Im chain at chain length L=1-5.](image)

The two kinds of planar complex arrangements (Figure 5.4) give an informative indication on the assignment of FTIR peak location. However, the extremely broad bandwidth cannot be explained by these simplified models. Since the C-H\(\cdots\)O hydrogen bond is a relatively weak interaction, it is reasonable to consider the frequency shift arising from rotational conformers along O-H\(\cdots\)N hydrogen bond. To investigate the existence of 3D rotational conformers, distribution on the angle between normal vector of C\(_1\)Im plane defined by hydrogen acceptor N and the two
adjacent C, and the normal vector of HAc plane defined by the carboxylate group COO, are calculated from AIMD trajectory.

Radial distribution function (RDF) between hydroxyl H in HAc and the hydrogen bond acceptor N in C\textsubscript{1}Im and its integral calculated from AIMD simulation are compared with previous AIMD results to check the reproducibility. Plots of RDFs are shown in Figure 5.6. There are two obvious solvation shell located at 0.95 Å – 1.35 Å and 1.35 Å – 2.25 Å, respectively. The first maximum locates at 1.05 Å, and the second is at 1.55 Å, which are all in agreement with previously published AIMD studies.[20]

![RDF plots](image)

Figure 5.6. Radial distribution function between hydroxyl H in HAc and the hydrogen bond acceptor N in C\textsubscript{1}Im and its integral.

From the normal vector angle distribution shown in Figure 5.7, instead of 0 and 180 degrees, the two maximums of distribution locate at 30 and 120 degrees at small x(HAc), or at 70 and 150 degrees at high x(HAc), which indicates two free energy minimums in hydrogen bond rotating coordinate. The structures at minimum energy are non-planar, which might result from the solvation shell energy stabilization. The carbonyl oxygen in HAc is energetically more favorable to form a hydrogen bond with another HAc in the solvation shell, compared with forming
C-H···O hydrogen bond with C$_1$Im. Besides, the broad distribution demonstrates the existence of 3D structure and free rotating along the hydrogen bond.

Figure 5.7. Distribution of AIMD frames on the angle between normal vectors of HAc and C$_1$Im plane at different x(HAc).

The existence of 3D conformers is also confirmed by the rotation energy surfaces calculated as a function of dihedral angle in different structures observed in AIMD. There are mainly two types of rotation. One is the rotation of C$_1$Im, the other is rotation of terminal HAc in the chain. 1HAc+1 C$_1$Im, 2HAc+1C$_1$Im, and 3HAc+1C$_1$Im structures were investigated as representative species in highly concentrated HAc solution. The energy surfaces along rotational coordinate of those representative structures are shown in Figure 5.8. Energy barrier of rotation is
found to be about 4 kcal/mol, which is possible to be overcome by thermal energy and local environmental energy variation. This result supports the existence of conformation change in the solution.

![Diagram](image)

Figure 5.8. Energy vs. dihedral angle. (a) HAc+ C1Im (black square); (b) 2HAc+ C1Im (red dot); (c) 3HAc+ C1Im (blue triangle); (d) HAc+ 2C1Im (magenta obtriangle); (e) HAc+ 2C1Im (green diamond).

DFT frequency computational results of two types of rotation in 2HAc+ C1Im, which is the most concentrated species in the conductive mixture, are shown in Figure 5.9 (a) and 5.11 (b). Results of C1Im rotation in HAc+C1Im, 3HAc+C1Im are displayed in Figure 5.9 (c) and (d). The hydrogen stretching mode maintains a strong absorption compared with other vibrational modes in all structures at all conformations. Frequency shift of ~300 cm\(^{-1}\) is observed in all cases, which indicates that the variance of conformation explains the homogenous broadening component of the broad band in FTIR spectra.
Figure 5.9. DFT frequency calculation of conformers in different complexes: (a) 2HAc+ C1Im; (b) 2HAc+ C1Im; (c) HAc+ C1Im; (d)3HAc+ C1Im.
There is one more question on the assignment of the FTIR peaks. From Figure 5.2(b), it is observed that even at x(HAc)=0.01, the 1900 cm\(^{-1}\) and 2500 cm\(^{-1}\) peak still exist, and the intensity ratio between those two remains exactly the same at low concentration from X(HAc)=0.1 to x(HAc)=0.01. Statistically, at such concentration, the probability of two HAc meeting to form L=2 chain is negligible. In terms of chemical equilibrium, as x(HAc) decreases, the equilibrium shifts to L=1 side, with changes of concentration ratio between L=1 and 2. This indicates that there are other structures in this diluted solution contributing to the 1900 cm\(^{-1}\) and 2500 cm\(^{-1}\) infrared absorption. Since it is highly concentrated C\(_1\)Im solution, structures of one HAc bonded with two and three C\(_1\)Im molecules were considered. Solvation shell structures of HAc obtained from AIMD are investigated to seek for the possible complexes existing at small x(HAc).

Distributions of number of carbonyl C (in HAc, denote as CT) and the number of C (between two N in C\(_1\)Im, denote as CR) in the first solvation shell of CT are calculated. RDF among CT is computed to determine the solvation shell cutoff and shown in Figure 5.10 (top). RDF at three molar fractions all have the first solvation shell within 4.85 Å, the second solvation shell at ~6.8 Å, followed by the third solvation shell. An extra sharp peak appears in the range of 3.5-4.0 Å at x(HAc)=0.02, and decreases fast as x(HAc) increases. Looking into the AIMD trajectory, this peak arises from the structure that one HAc stacks on top of another, forming two parallel layers (a snapshot inserted in Figure 5.10). The C\(_1\)Im in the solvation shell of HAc might block the formation of this structure. From the integrated g(r), increasing number of HAc at the cutoff 4.85 Å is observed as the increase of x(HAc). 2.2, and 3.3 HAc are found to exist in the first solvation shell at x=0.67 and 0.85 respectively, and coordination number of 4 is found at x(HAc)=0.99 and 1.0.
RDF between CT and CR are also calculated and plotted in Figure 5.10 (bottom). The first minimum is located at 4.85 Å, which is the same position as the minimum of RDF between CT and CT. The second minimum is located at 7.25 Å, indicating a thicker second solvation shell composed of C$_1$Im compared with that composed of HAc. This difference can be explained by the larger volume/radius of C$_1$Im compared to HAc. The number of C$_1$Im in the first solvation shell is 0.1, 0.6, 1.4, and 3.0 at $x$(HAc)=0.99, 0.85, 0.67, 0.02. Therefore, in very diluted HAc solution ($x$(HAc)=0.02), there are 3 C$_1$Im molecules in the first solvation shell of HAc on average, indicating a big amount of 1HAc+2C$_1$Im and 1HAc+3C$_1$Im complexes existing in the diluted solutions.

Figure 5.10. RDF and its integral between CT and CT (top), CT and CR (bottom).
In addition, the integrated g(r) shows the number of C1Im in first solvation shell of HAc decreases as the increasing of x(HAc). This indicates as x(HAc) increases, HAc molecules come into the first solvation shell while C1Im molecules are leaving from the first solvation shell.

Similar to HAc chain terminated with C1Im, different spatial arrangements of 1HAc+2C1Im and 1HAc+3C1Im complexes due to the formation of C-H···O hydrogen bond are all investigated. Calculated frequencies are shown in Figure 5.12 and the corresponding structures in Figure 5.13. It can be observed from the plot that 1HAc+2C1Im structure has an absorption at 1800 cm⁻¹ (Figure 5.12(b) and 5.12(b)) with high intensity, and 1HAc+3C1Im structure produces two high-intensity IR absorption at ~2300 cm⁻¹ (Figure 5.12(e-f) and 5.12(e-f)). Therefore, it can be assumed that at small x(HAc), the absorption centered at 1900 cm⁻¹ can be assigned to proton stretching of 1HAc+2C1Im structure, and the absorption centered at 2500 cm⁻¹ can be assigned to proton stretching of 1HAc+3C1Im structure. The unchanged ratio between those two peaks at different x(HAc) indicates that the two structures have same Gibbs free energy. The energy change of breaking C-H···O hydrogen bond between HAc and the third C1Im can be compensated by the energy change of hydrogen bond network rearrangement in the solvation shell of HAc.

Conformations of these dominant species in diluted HAc solution are investigated to understand the broad infrared peaks. 1HAc+2C1Im and 1HAc+3C1Im complexes in Figure 5.14(b) and 5.14(f) are taken as representative species. The energy surfaces of rotation along hydrogen bond are shown in Figure 5.8(d) and 5.8(e), where the energy barrier is on the same order of thermal energy. Histogram of the number of nitrogen in the first solvation shell of carbonyl carbon in the diluted HAc solution shown in Figure 5.11 (top left) confirms the existence of 1HAc+2C1Im and 1HAc+3C1Im complexes at small x(HAc). DFT frequency calculations are performed on the conformations of these two complexes rotating along the hydrogen bond, and the results are shown.
in Figure 5.14. Frequency shifts of ~300 cm\(^{-1}\) are observed for the two complexes, which is responsible for the FTIR broad bandwidth.

![Histograms](image)

Figure 5.11. Histograms of number of carbonyl C (bottom) and N (top) in the first solvation shell of C.

Based on DFT calculation and FTIR study, it can be assumed that at x(HAc)<0.1, the dominant species in mixture that responsible for the broad bands are 1HAc+2C\(_1\)Im (1800 cm\(^{-1}\)) and 1HAc+3C\(_1\)Im (2300 cm\(^{-1}\)), and their concentrations increase as x(HAc) increases. In molar fraction range 0.1<x(HAc)<0.65, the dominant species are 1HAc+1C\(_1\)Im (2300 cm\(^{-1}\)) and 2HAc+1C\(_1\)Im (1800 cm\(^{-1}\) and 3000 cm\(^{-1}\)). At x(HAc)>0.65, 2HAc+C\(_1\)Im chains and longer chains become two competing components in the mixture.
Figure 5.12. DFT frequency calculation results of HAc and C1Im complexes.

Figure 5.13. Structures of complexes taken in DFT frequency calculation.
5.4.2. Delocalization of protons from computational calculation

The coordinate of proton motion in the proton stretching mode investigated by DFT calculation before is the same as the coordinate of proton delocalization. It can be observed from the DFT calculation results that proton between HAc and C\textsubscript{1}Im is delocalized. When the HAc chain gets longer, a second delocalized proton appears between the first and second HAc. The third delocalized proton appears at L>3.

Radial distribution function between hydroxyl H in HAc and the hydrogen bond acceptor N in C\textsubscript{1}Im and its integral are shown in Figure 5.6. There are two obvious solvation shells, which are in agreement with the previous AIMD studies.[20] The first solvation shell is corresponding to the delocalized protons which deviate from the initial positions near oxygen. Previous Raman study supports this assignment with the fact that the ions are negligible in this mixture.[16] The
second solvation shell composes of the protons on the O side. The two solvation shells are overlapped without any zero probability point in between, which proves proton delocalization. Integrated g(r) gives the ensemble average number of H in the first solvation shell of N to be 0.79, 0.45, and 0.1 at x(HAc)=0.86, 0.67, and 0.02 respectively. This strongly supports the existence of proton delocalization in all molar ratio of mixtures and indicates that at least 79% and 45% of protons in C1Im -HAc complexes are delocalized. The two states of protons can also be observed from the trace of OH distance in the AIMD trajectory in Figure 5.15. However, the statics results from our simple canonical ensemble MD simulation only give information on free energy and remove the influence from entropy change of the system. To remove the effect of entropy, DFT calculation at T=0 K is needed.

![Figure 5.15. Trace of OH distance in 4 trials in the mixture at x(HAc)=0.02.](image)

The energy surface of scanning the proton from the oxygen side to the nitrogen side is calculated by Gaussian 16. Energy surfaces of the 1st proton in pure HAc-HAc dimer chain, HAc-C1Im chain, and HAc-HAc- C1Im chain are compared in Figure 5.16(a). Proton is confined in a narrow single well close to oxygen in the HAc dimer chain. When C1Im replaces one HAc
molecule, energy at $r(\text{OH})=1.5\,\text{Å}$ decreases from $\sim30\,\text{kcal/mol}$ to $\sim4.7\,\text{kcal/mol}$, forming a second energy minimum close to the nitrogen atom. Taking account of the estimated zero-point vibrational energy of the proton vibrational motion, which is about $5.4\,\text{kcal/mol}$, the same scale as the energy difference between the two local minimums, the proton can be considered to be in a state that it moves back and forth freely from the oxygen side to the nitrogen side. This delocalized quantum state is neither a mixture of simple acid and base molecules (HAc and C$_1$Im), nor a mixture of two ions (Ac$^-$ and HC$_1$Im$^+$), as the previous classical understanding of the system. In fact, the solution is composed of HAc-C$_1$Im complexes at different chain lengths, whose H-bonded proton is delocalized, and the excess HAc or C$_1$Im as a solvent. It’s the first time that proton delocalization with a neutral complex formation is observed in a simple mixture of two types of molecules, which can be utilized in chemical reactions such as polymerization.

Pump-probe spectroscopy results confirmed the existence of proton delocalization with the obvious inversed anharmonicity, which can only come from a flat-bottom steep potential well of the delocalized proton.[1, 2]

Based on the discussion in the last section and previous studies, [20, 35] the HAc/C$_1$Im mixture adopts a Grotthuss-like proton conduction mechanism, which in this case indicates that the delocalized proton initiates the Grotthuss-like conduction mechanism. The proton delocalization can explain the overlapped $\chi(\text{HAc})$ position of the viscosity maximum and the Walden product maximum. At the maximum of Walden product, there exists the highest concentration of charge carrier, which is the delocalized proton. As a result, the concentration of HAc- C$_1$Im complexes reaches its maximum, leading to the strongest overall intermolecular interaction and hydrogen bond network, and thus a maximum of viscosity.
Figure 5.16. Potential energy surfaces of different complexes on proton stretching coordinate.

Looking back into Figure 5.16(a), compared with HAc+ C₁Im structure, 2HAc+ C₁Im displays an even lower potential energy of around 1.7 kcal/mol at r(OH) = 1.45 Å. Considering the zero-point vibrational energy and thermal energy, 2HAc+ C₁Im has a barrierless flat-bottom potential well. As the energy barrier decreases, which means proton gets more delocalized, the minimum position at the oxygen side shifts further away from oxygen from r(OH)=1.00 Å to 1.10 Å, while the second minimum near N shifts from N to O at the same time from r(OH)=1.6 Å to 1.45 Å, demonstrating the delocalized proton prefers to distribute in the middle area between O and N, instead of the local position close to O or N. The comparison among different structures indicates that forming a hydrogen bond with a C₁Im molecule delocalizes the acid proton, and increasing of the chain length L helps to stabilize the delocalized proton.

The influence of different spatial arrangements on proton delocalization is investigated and plotted in Figure 5.16(b). The energy surface of 1st proton in 2HAc+ C₁Im complex is modified by the structure while it’s barrierless in both structures. In the linear complexes, the energy minimum is located close to the oxygen side. In the cyclic complexes, the minimum shifts to the
position close to the nitrogen side. Meanwhile, the second proton is localized in the linear structure and a lot more delocalized in the cyclic structure.

From the AIMD trajectory, it is observed that structures of $2\text{HAc} + C_1\text{Im}$ and $3\text{HAc} + C_1\text{Im}$ have a much higher concentration compared with other complexes at the $x(\text{HAc})$ of maximum conductivity. It can be inferred that the concentration of $2\text{HAc} + C_1\text{Im}$ and $3\text{HAc} + C_1\text{Im}$ determines the Walden product. This is because the delocalized proton in these structures has a flat-bottom barrierless potential well as shown in the last part, so the protons can vibrate from O side to N side, initiating the Grotthuss-like mechanism. Thus the concentration of $2\text{HAc} + C_1\text{Im}$ and $3\text{HAc} + C_1\text{Im}$ complexes determines the conductivity.

### 5.5. Summary

In the system of acetic acid and methylimidazole mixture, solvation structure and dynamics were investigated by linear the non-linear spectroscopies and computational calculation. The high-absorption broad-band peaks in infrared spectroscopy were assigned to proton stretching mode in $\text{HAc}/C_1\text{Im}$ complexes. Dominant species at high $x(\text{HAc})$ were demonstrated to be $\text{HAc}$ chain ended with a $C_1\text{Im}$ terminal molecule, while the dominant species at very low $x(\text{HAc})$ were found to be $\text{HAc}+2C_1\text{Im}$ and $\text{HAc}+3C_1\text{Im}$ complexes. Conformers of complexes arising from rotation around hydrogen bonds were proved to exist and are responsible for the large bandwidth of proton stretching mode in infrared spectroscopy. The most impressive finding is the existence of proton delocalization. A flat-bottom potential energy surface of proton stretching is obtained from both DFT calculation and pump-probe experiment, which proves the existence of proton delocalization in the hydrogen bond between $\text{HAc}$ and $C_1\text{Im}$. It is the first time that proton delocalization is observed in a simple mixture of two molecules. This project provides a new method to generate
proton delocalization and start a polymerization by mixing a weak acid and a weak base with similar proton affinity.

5.6. References


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167
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