Effects of Micro-Solvation on Room Temperature Ionic Liquids

By:

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ABSTRACT

Joseph Wellington Golden: Effects of Micro-Solvation
on Room Temperature Ionic Liquids
(Under the direction of Dr. Nathan Hammer)

Room temperature ionic liquids (RTILs) have received much attention lately. These compounds are made completely of ions and are liquid at or near room temperature. These liquid salts have a number of unique properties that make them an interesting system to study. These properties include almost zero vapor pressure, thermal stability, large liquidus range, etc. Due to these properties and others, ionic liquids (ILs) have attracted much attention in the emerging field of green chemistry as potentially new solvents for many of the hazardous and volatile solvents currently in use. Moreover, the complex interactions of the anion and cation systems of the room temperature ionic liquids have been shown to participate in hydrogen bonding, and the addition of hydrogen bonding compounds (i.e. water, methanol, etc.) have been reported to alter many of the properties of ILs. Many ionic liquids are hygroscopic by nature so the addition of water to the system can occur readily from the atmosphere. Thus, the study of the effects of water or other solvents on the microscopic nature of the RTILs is of importance since it can affect many of the bulk properties of the RTILs. In this thesis, we explored the complex intermolecular interactions through the use of spectral data via Raman spectroscopy and computational data of the RTILs of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, 1-(1-butyl)-1-methylpyrrolidinium bis(trifluoro-methanesulfonyl)imide, and 1-butyl-3-methylimidazolium dicyanamide.

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1 Introduction

1.1 Ionic Liquids

Over the past decade, there has been a vast growth in the interest of room temperature ionic liquids (RTILs) and some believe this period to be a renaissance for ionic liquids (ILs), where ILs are a broader class composed of liquid salts that melt below 100^{o}C.[1] RTILs are a class of compounds that have the unique property of being liquid at or near room temperature while being composed entirely of ions.[2] Since these RTILs are composed of solely of ions, these liquids possess many interesting physiochemical properties, such as a non-volatile nature, high electrical conductivity, a low melting point, thermal stability, and almost zero vapor pressure, that make them particularly interesting as potential solvents.[3-7] Moreover, ILs have the unique property of being tunable. Interestingly, many of the physical properties of ILs, such as their miscibility with other compounds, melting point, viscosity, and etc, are able to be selected for desired properties by changing the ion combinations.[9] For example, selecting an anion with the positive charge delocalized and a cation with a shielded positive charge have been shown to lower the melting point of the IL due to a decrease in the Coulomb interactions between the two ions.[10] Furthermore, an ion with low symmetry can also disrupt crystallization; this would make the salt have a lower melting point..[11] Another example is seen with ammonium-based ionic liquids. By incorporating ammonium cations with alky chains that vary in length, the resulting salt possessed a lower melting point than the

salts with symmetric ammonium cations.[12] Similarly, it has been shown that by changing the anion of the IL many of the liquid phase properties of the IL can be modified. These liquid phase properties include density, viscosity, miscibility with organic compounds, etc..[13-16] There are numerous possible combinations of cations and anions for an ionic liquid, and it has been estimated that there are around 10^{18} possible ionic liquid combinations.[8] Figure 1 lists some of the most common ions utilized in the field of ionic liquids. However, many of the bulk properties are not as predictable as the examples provided above, and in order to understand and predict many of the bulk properties of ionic liquids, a firm understanding of the microscopic factors that influence the microscopic and bulk properties of ILs is still needed.

One of the major reasons ILs are being explored in detail recently is due to their potential as solvents in the green chemistry field. ILs are being explored and employed as "green" substitutes for volatile organic solvents since ILs themselves are essentially non-volatile. One of the major reasons ILs are being explored as potential solvents is due to the huge liquidus range. This range is the extent of temperatures between the freezing and boiling of liquid in question. This liquidus range and numerous other solvent properties of ILs allow for them to be the ultimate non-volatile organic solvent. Molten polymers are the only other known solvent that can rival the low volatility of ionic liquids.[1]

Ionic liquids have an interesting history that can be dated back to the 19th century. As mentioned and for the purposes of this thesis, an ionic liquid is going to be defined as a salt possessing a melting point below 100^{o}C (or rather below the point at which water boils). Ionic liquids as defined have numerous synonyms in the literature that can, unfortunately, complicate literature searches. These synonyms include room temperature molten salts, low temperature molten salts, ambient temperature molten salts, ionic fluids, and liquid

organic salts, and may even be referred to as a neoteric solvent (referring to this older material finding new application as solvents).[1]

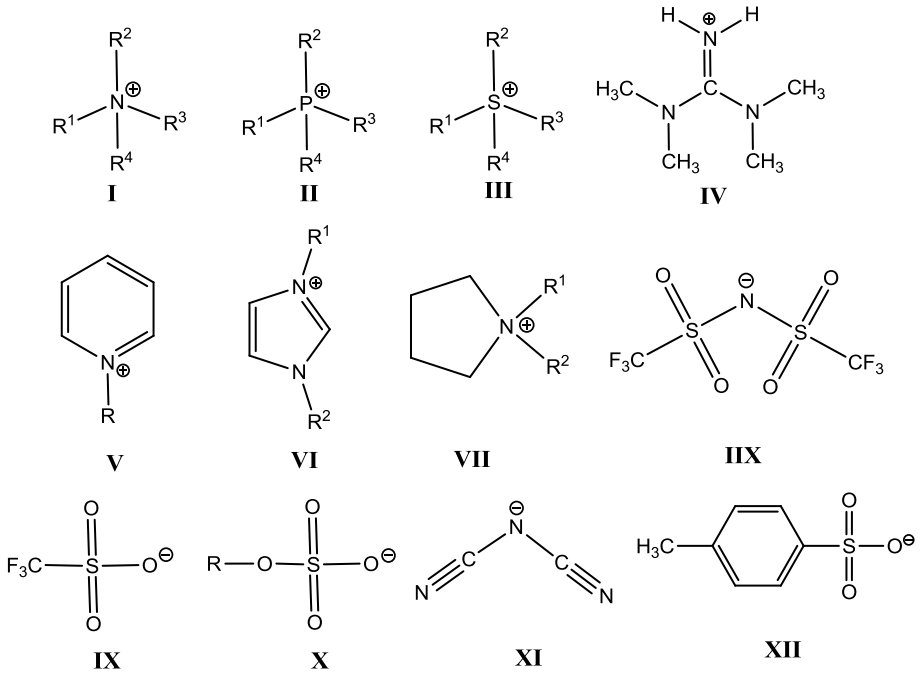

Figure 1. Shows some of the most common ions used for ionic liquids. Common Cations: **I**: tetraalkylammonium; **II**: tetraalkylphosphonium; **III**: tetra-alkylsulfonium; **IV**: guanidinium; **V**: 1-alkylpyridinium; **VI**: dialkylimidazolium; **VII**: 1,1-dialkylpyrrolidinium. Common anions: **IIX**: bis(trifluoromethane-sulfonyl)amide; **IX**: trifluoromethanesulfonate; **X**: alkylsulfates; **XI**: dicyanimide; **XII**: tosylate.

Interestingly, the first ionic liquid that was documented occurs during Friedel-Crafts reactions in the mid-19th century. The model Friedel-Crafts reaction is the reaction catalyzed by a Lewis acid (such as $AlCl_3$) where a benzene acts as the substrate and chloromethane reactants to yield toluene. This reaction typically yields a red-colored phase, which was not identified until NMR became widely available. As shown in Figure

2, this red liquid was eventually identified as heptachlorodialuminate salt where the cation in the salt is the stable intermediate known as the sigma factor.[1]

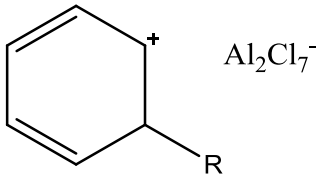

Figure 2. Heptachlorodialuminate

In the early 20th century, alkylammonium nitrates were discovered to be liquids. For example, Ethylammonium nitrate ($CH_3CH_2NH_3^+NO_3^-$) possesses a melting point of 12°C. In the navy's search for liquid propellants, the more complicated nitrates were later discovered to be ionic liquids. A professor at Oregon State University named John Yoke found mixtures of copper(I) chloride and alkylammonium chlorides during the 1960s. These salts were liquid close to room temperature. In the 1970s, Prof. Jerry Atwood and his research group at the University of Alabama found liquid clathrates that are now recognized as ionic liquids. Liquid clathrates are composed of an aluminium alkyl with a salt and forms a compound with one or multiple aromatic molecules.[1]

$$M[Al_2(CH_3)_6X] + n\text{Aromatic} \xrightarrow{\text{High Temp.}} M[Al_2(CH_3)_6X] \cdot n\text{Aromatic}$$

Figure 3. Liquid clathrate compound

Many of the current ionic liquids that are popular (such as the heterocyclic cations of alkylpyridinium or dialkylimidazolium) can be traced back to the inorganic chloroaluminates. Chloroaluminates are often considered the first generation ionic liquids

and were commonly called low temperature molten salts. The original intention of studying chloroaluminates was in their potential application for thermal batteries and much of the research was conducted by the U.S. Air Force. Thermal batteries possess a molten salt electrolyte (such as LiCl-KCl) and once started is usually heated to temperature ranging from 375 to 550^{o}C. The high temperatures can obviously cause problems and, thus, is why the Air Force Academy searched for a salt electrolyte that had a lower melting temperature. Dr. Hussey, who is currently the Chair of the Chemistry department here at the University of Mississippi, actually conducted much of the research in characterizing electroactive materials in inorganic chloroaluminate molten salts, and his research helped result in a patent for a thermal battery with a NaCl–AlCl3 electrolyte.[1]

With the discovery of 1-butylpyridinium chloride – aluminium chloride mixture (BPC–AlCl3), the start of the modern era of ILs began; however, there are a few unfortunate features of this IL—a melting temperature of 40^{o}C, the butylpyridinium cation is easily reduced resulting in a narrower electrochemical window compared to NaCl—$AlCl_3$, and an incompatibility with silver electrodes. Thus, the search continued for a salt with an even a lower melting temperature.[1]

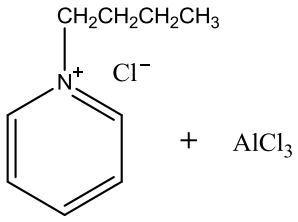

Figure 4. 1-butylpyridinium chloride – aluminium chloride mixture.

In the search for an IL with a lower melting temperature, several principles were utilized to help select a better anion/cation system. It was figured that large anions possessing many degrees of freedom, large cations paired with large anions, and asymmetric cations all should result in salts with lower melting temperatures. With the help of Utilizing MNDO calculations (Modified Neglect of Differential Overlap), several compounds were able to be considered for a potential salt with a low melting temperature. One of the compounds tested was the dialkylimidazolium which is shown in Figure 5. These dialkylimidazolium compounds now represent one of the most common cations chosen for ionic liquid systems such as the 1-ethyl-3-methylimidazolium cation. [1] In 1990, many combinations of ions that formed air-stable and water-stable combinations were found, and ILs have since then found numerous applications in academia and industry.[17] To name a few of the applications, ILs are found in high-temperature fuel cells,[18-19] lithium batteries,[20-22] and dye-sensitized solar cells[23-25]. The increasing use of ILs in the world demands a firm understanding of the unique interactions that occur among cations and anions of ILs as well as a firm understanding of the interactions that occur between ILs and solvents, such as water

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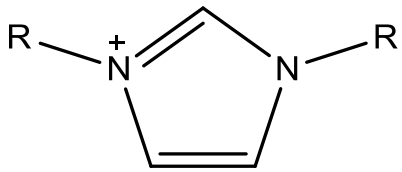


Figure 5. A diagram of the dialkylimidazolium cation

1.1.1 Anion-Cation Interactions involving RTILs

In order to understand and predict the bulk properties of RTILs, there must be a thorough understanding of the interplay of the complex interactions occurring in the ILs, namely the Coulomb and dispersion interactions of the anion-cation system. In quantum chemistry, long-range interactions refer to interactions through space that do not require an orbital overlap. These kinds of interactions include Coulomb, π-π stacking, and van der Waals interactions. Conversely, intermolecular interactions are considered short-ranged if there is an orbital overlap between the interacting compounds. Hydrogen bonding is included within the short-range category. In the ionic liquid field, long-range interactions usually refer to those that decay slowly with increasing distance between ions (proptional to 1/R), such as Coulomg interactions, whereas inter-ionic interactions that decay much faster with increasing distance (proportional to $1/R^6$) are referred to as short-range interactions. Long and short both refer to the distance and not the nature of the interaction in question.[11]

The liquid character of ILs with melting temperatures much lower compared to inorganic salts such as NaCl are due to the long-range Coulomb interactions and the short-range dispersion interactions between the cations and anions.[11] Generally, Coulomb interaction in RTILs play the major role for the interactions. This is in contrast to the situation of ordinary molecular liquids where only dipolar and/or higher order multipolar electrostatic interactions mainly occur. Since the Coulomb force is long-range in nature, the melting points of salts are much higher than those of other molecular crystals. With that in mind, the RTILs are extraordinary with their low melting points.[2]

Ionic liquids possess interesting molecular interactions that result from both their geometry and charge distribution. Many of the simpler salts have interactions that result from long-range coulomb forces between the ions. Salts of greater molecular size begin to exhibit softer coulomb forces and directional interactions of shorter range due to a bulkier nature along with an asymmetric charge distribution. Equation 1.1 summarizes the forces at work. It shows that the interaction potential (U) depends on distance (r) of the ions and the angles (W) for their mutual orientation. Electrostatic, inductive, and van der Waals (dispersive/repulsive) interactions are all utilized in the equation as can be seen. Equation 1.1 can also can also include specific interactions such as hydrogen bonding but usually is not necessary since many hydrogen bonds are electrostatic.[17]

$$U(r,W) = U_{es}(r,W) + U_{ind}(r,W) + U_{vdW}(r,W) \qquad (1.1)$$

The electrostatic term can also be broken down into interactions that occur between ions, dipole moments, and higher electrostatic interactions as shown in Equation 1.2.

$$U_{es}(r,W) = U_{ion\text{-}ion}(r) + U_{ion\text{-}dipole}(r,W) + U_{dipole\text{-}dipole}(r,W) + U_{ion\text{-}quadrupole}(r,W)... \quad (1.2)$$

In most molecular liquids, dipole-dipole interactions are the strongest interaction and this interaction essentially controls the salvation capability of the liquid. However, due to the net charge of ILs, the understanding of electrostatic interactions of ILs is complicated. Charge neighbors screen the electrostatic interactions of nearby ions from

other particles farther away. For simpler salts, such as NaCl, screening of the Coulomb forces between ions forms the basis of how we understand liquid-phase properties. Screening affects all of the electrostatic interactions shown in Equation 1.2. This screening localizes the electrostatic interactions and has caused some rethinking of the basic concepts of salvation in ionic liquid system. Normally, solvation concepts are based on a continuum approximation for solvents.[17]

ILs generally have significantly reduced Coulomb interactions due to the shielding and delocalization of the charge in ionic compared to inorganic salts. This reduction of electrostatic interactions is allows for the observed lower melting points lower ILs. It was shown by Madelung that in inorganic salts the Coulomb interactions (both attractive and repulsive) converged to a number known as the Madelung constant (M). Therefore, the electrostatic lattice energy of an inorganic salt, E_{es}, can be expressed as shown in Equations 1.3 where d_{min} is the distance to the nearest counter-ion .

$$E_{es} = Mq_{cation}q_{anion} / 4\pi\varepsilon_0 d_{min} \qquad (1.3)$$

The electrostatic binding energy of a single ion pair, E_{es}^{IP}, the lattice energy can be expressed as shown in Equation 1.4.

$$E_{es} = ME_{es}^{IP} \qquad (1.4)$$

Hence, the Madelung constant can be thought of as the degree that the lattice of ions is more stable than the isolated collection of ion pairs. For stable crystal structures M

> 1 and the larger M is, the more stable the crystal structure will be. As expected due to ILs melting points, the Madelung constant has been calculated for several organic ionic salts to be at 25% lower than that of NaCl. [11]

The inclusion of organic substituents result in the reduction of the electrostatic interactions. This means that it is expected that the dispersion-type (i.e. non-electrostatic) interactions can play an important role in interactions of ILs. Other than the obvious dispersion interactions of van der Waals between alkyl chains, the dispersion interactions in a single ion pair has been found to contribute significantly. It has also been found through crystal structures that same-charged species can also add to the stability of ILs. [11]

1.1.2 Intermolecular Interactions involving RTILs

Understanding the intermolecular interactions of room temperature ionic liquids with other species is of great importance. Ionic liquids (ILs) constitute a promising class of technologically useful and fundamentally interesting materials. The uses of ionic liquids range from environmentally friendly solvents for novel chemical synthesis, to electrolyte devices, such as batteries and photochemical cells. For any application of ionic liquids, the physical properties are a key feature. Meanwhile, there is increasing interest in changing the physicochemical properties of ILs simply by mixing them with conventional molecular liquids. However, the transport properties such as diffusivity, viscosity and conductivity do not change linearly with the concentration of the solute and solvent. To characterize the mixing behavior, understanding of the mixtures at the molecular level is mandatory.[26] For example, the presence of water in many RTILs have been shown to affect many of their solvent properties such as polarity, viscosity, density, and conductivity. Even RTILs that are commonly referred to as hydrophobic have been shown to be hydroscopic and can absorb

water from the atmosphere.[11] The structure and properties of ionic liquids are mainly determined from Coulomb interactions between the anions and cations of the system. However, hydrogen bonds are of great importance in understanding RTILs since these forces can affect both the structure and properties of the system by forming extending hydrogen bonding networks.

Since ionic liquids are hygroscopic by nature, many ionic liquids absorb water from the air due to the humidity, and this absorption of water can have a number of affects on the anion/cation system.[17] The presence of impurities in the IL system can lead to observable changes in properties, such as density, internal structure, viscosity, polarity, and conductivity.[27-33] In addition, many applications involving ionic liquids require them to be mixed with other species. The presence of small amounts of water have been shown to drastically modify the rates and selectivity of reactions.[34-35] Due to the importance that interactions with other media can play on the properties of ionic liquids, the study of micro-solvated ILs is of particular interest. Raman spectroscopy and computational studies are employed in our investigations of micro-solvated RTIL systems.

The number of publications regarding the fundamental physical chemistry of ionic liquids in solvent systems is growing rapidly; there is now a wealth of information on ionic liquids that it can become quite difficult to get an accurate overview of the literature. The first studies dealing with intermolecular interactions focused with the first-generation chloroaluminate ionic liquids; however, these studies have now advanced to the air-stable, second generation ionic liquids. Numerous papers cover the theoretical aspects of the ionic liquid system as well as the viscosity, diffusion, gas solubilities, crystallography, etc data of the ILs.[36-53] There are equally numerous papers dealing with the interactions between water and ILs.[53-73]

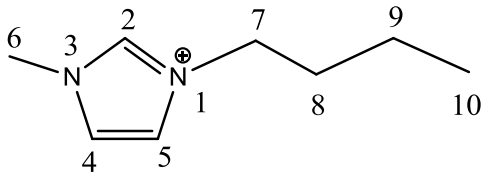


Figure 6. 1-butyl-3-methylimidazolium cation

It has been reported that hydrogen-bonding occurs in most ionic liquids between the cations and anions. In 1-alkyl-3-methylimidazolium, all three of the hydrogens on the ring (H2, H4, and H5) have been shown to participate in strong hydrogen bonds.[74-79] Huang et al. has reported that H2 hydrogen is attached to the anion $[BF_4]^-$ in neat 1-ethyl-3-methylimidazolium tetrafluoroborate $[C_2mim][BF_4]$ ionic liquids.[80] This was later confirmed using IR and Raman spectroscopy.[81] Furthermore, the degree of hydrogen bonding, and thus the degree of miscibility, changes based on the anion. This was demonstrated between neat chloride and hexafluorophosphate mixtures. With IR spectroscopy and by comparing 1-butyl-3-methylimidazolium hexafluorophosphate $[C_4mim][PF_6]$ and 1-butyl-3-methylimidazolium tetrafluoroborate $[C_4mim][BF_4]$, it was found that water forms stronger hydrogen bonds with $[BF_4]^-$ anion over that of the $[PF_6]^-$ anion. Similarly, utilizing near-infrared (NIR) spectrometry, it was found that 1-butyl-3-methylimidazolium liquids absorbs water and this absorption is varied based on the anion chosen. They found that borontetrafluoride ($[BF_4]^-$), bis(trifluoromethylsulfonyl)imide ($[Tf_2N]^-$), and phosphoroushexafluoride ($[PF_6]^-$) anions interacted with water in decreasing order, respectively. [76-79] Hence, the anion plays a pivotal role in the miscibility and strength of hydrogen bonds as was discussed earlier.

Mixtures of ILs and molecular solvents have also been investigated extensively both experimentally and theoretically.[36-73] Bowers et al. has performed surface tension, conductivity, and small-angle neutron scattering (SANS) measurements on ionic liquids and has observed aggregation behavior of 1-butyl-3-methylimidazolium tetrafluoroborate $[C_4mim][BF_4]$, 1-octyl-3-methylimidazolium chloride $[C_8mim][Cl]$ and 1-octyl-3-methylimidazolium iodine $[C_8mim][I]$ in aqueous solutions.[82] Studies of the liquid–liquid equilibrium between of IL and alcohol solutions have shown a significant dependence on the length of the alkyl-chain for the imidazolium cations of ionic liquids.[83-84] Takamuku et al. studied, through small-angle neutron scattering (SANS) experiment, the mixtures of 1-ethyl-3-methylimidazolium chloride $[C_2mim][Cl]$ with methanol and with acetonitrile. They have also studied the IL system of 1-ethyl-3-methylimidazolium bis(trifluoro-methylsulfonyl)imide $[C_2mim][NTf_2]$ with methanol and benzene.[85] Shimomura et al. looked at the effects that alkyl-chain length had on the mixing state of solutions with imidazolium-based IL and methanol.[85] From SANS, attenuated total-reflectance infrared (ATR-IR), and NMR techniques, Shimomur et al. reports a maximum heterogeneously mixing of methanol at the mole fraction range of X_{MeOH} = 0.8–0.995. In this range, they did not observe any characteristic alkyl-chain length dependence for the imidazolium cation. However, above X_{MeOH}=0.8 Shimomura et al. found an increasing concentration of self hydrogen bonding of the methanol molecules.

L. Cammarata et al. looked at the interaction of water on the ionic liquids with 1-butyl-3-methylimidazolium as the cation and $[PF_6]^-$, $[SbF_6]^-$, $[BF_4]^-$, $[ClO_4]^-$, $[CF_3SO_3]^-$, $[NO_3]^-$, and $[CF_3CO_2]^-$ as the anion via infrared spectroscopy.[87] If the liquids were left open to the atmosphere, they found growths in the IR modes of water and contributed this

to the absorption of water from the atmosphere. Moreover, the authors found that most of the water absorbed from the atmosphere hydrogen bonded with both hydrogen atoms of the water and to two anions of the RTIL (i.e. anion···H–O–H···anion). Cammarata et al. also found that H_2O can form aggregates in the ionic liquids. Thus, the anions were found to play the major role in the solubility and miscibility of water molecules in ionic liquids studied and that the cations play a secondary role. This means that the acidic protons on the imidazolium ring does not play a direct role in water absorption and hydrogen bonding. Thus the absorption of water from the atmosphere is in direct correlation with the strength of the H-bonding interactions with the anion (meaning that different anions will affect the absorption of water).[87]

As opposed to other work, J. Andanson et al. found good molecular mixing among ILs and water and the absence of nanosegregations as other works have found.[88] K. Fujii et al showed via Ramana spectroscopy and DFT calculations that the anion bis(trifluoromethanesulfonyl)imide ($TFSI^-$) possess different comformations and this equilibrium between the two conformers can be detected in the strong $TFSI^-$ bands at 398 and 407 cm^{-1}.[88] This conformation equilibrium is affected by the temperature of the system with one conformation being more favorable than the other.

Molecular dynamics (MD) simulation have also been greatly utilized in the efforts to study ILs in molecular solvents. Lopes et al. has investigated the type and strength of interaction between the IL $[C_4mim][PF_6]$ with molecular solvents n-hexane, acetonitrile, water and methanol.[89] Jiang et al. simulated aqueous solutions of the IL $[C_8mim][NO_3]$ to investigate the nanostructural organization of the mixtures in water-rich regions. They reported that up to $X_{H2O} = 0.8$ of the water molecules interact as donors with the NO_3^-

anion, and that further increase in water concentrations caused an greater formation of water clusters. Jiang et al. reported that the micelle structures formed in the solution are only barely present in the IL due to the dominant water–water interactions in the high concentrations of water.[90]

Roth et al. conducted very interesting experiments that are particularly pertinent to what we hoped to do. They studied in detail the molecular interactions of the hydrophobic RTIL of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C_2mim][NTf_2] mixed with methanol.[26]. C. Roth et al. explored the [C_2mim][NTF_2] IL mixed with methanol due to methanol's amphiphilic character and miscibility with RTIL over the whole mixture range. Deuterated methanol (CD3OD) was used to avoid overlap between the O-H stretching bands of methanol and the alkyl stretching bands of the imidazolium cation. Roth et al. found that the addition of methanol to the neat IL system caused interactions to occur between the OD groups of the organic solvent and the proton acceptor S=O groups of the $[NTf_2]^-$ anion. They further reported that this methanol–anion interaction is weaker compared to the methanol–methanol H-bond interactions found in the larger methanol clusters. They found the OD vibrational mode at 2650 cm^{-1} to be significantly shifted to higher wavenumbers compared to the neat methanol contributions, as expected due to the hydrophobic character of the $[NTf_2]^-$ anion. Up to X_{MeOD} = 0.8 the methanol molecules preferentially occupied four acceptor positions before they observed the formation of pure alcohol clusters. The dynamical heterogeneities were found to decrease and the diffusivity of methanol was found to increase with the increasing H-bond formation of methanol. At methanol concentration of $>X_{MeOD}$=0.9, the mixtures were found to become more fluid and adopt properties more similar to pure methanol. In

these highly concentrated methanol mixtures, the IL was found to exist as ion-pairs or neutral aggregates of ion-pairs in the methanol environment. A final conclusion from their work was that both types of methanol molecules present in methanol–methanol clusters or in methanol–anion configurations could be characterized by distinct dynamical heterogeneities.[26]

There are an abundant number of other papers not mentioned here that deal with the interactions of RTILs. The papers summarized here are meant to provide a rough overview of the vast wealth of information available dealing with ILs and to summarize the papers deemed particularly important to the work of this paper– to help explain the complex interactions occurring between RTILs and hydrogen-bonding solvents. Other interesting papers that deal with the complex interactions of ionic liquids are included in [References 91-108] for the interested reader.

1.2 Spectroscopy

1.2.1 Introduction

Simply put, spectroscopy is the study of interaction between electromagnetic radiation and matter. We know from quantum mechanics that energy is essentially just a form of matter and, thus, can interact with matter for that very reason. Molecules can rotate, vibrate, and translate, and when radiant energy (light) interacts with matter, these motions can be affected. Light and matter can also interact to promote an electron to a higher state, known as an electronic transition. Hence, the interaction between matter and light can affect the spin, rotation, vibration, and electronic state of matter.[109]

Since transitions occur between quantum states, the energy of the incident radiation is extremely important for observing transitions. The energy of a photon is directly related to frequency (ν) and Planck's constant (h) as shown in Equation 1.5.[109]

$$E = h \nu \qquad (1.5)$$

Thus, the frequency of the incident radiation is important in determining the energy of the photon and, thus, what discrete transitions can occur. Figure 1 shows the different regions of the electromagnetic spectrum with radio waves possessing the least amount of energy and gamma rays possessing the greatest amount of energy based on their corresponding frequencies. Later, it will be discussed what regions of the electromagnetic spectrum contain enough energy for the observation of the different types of transitions.[109]

Several things can occur when light strikes matter. The light can be absorbed, transmitted, reflected, or scattered by the sample and many of these processes are taken advantage of in spectroscopy. Moreover, luminescence can also occur in the sample (i.e. light is emitted from the sample after absorbing light).[109]

We also know from quantum mechanics that molecules can only exist in certain discrete states with discrete energy. Thus, for a transition to occur a photon with the exact energy for the transition must be absorbed which is why the frequency of the incident radiation is particularly important.[109]

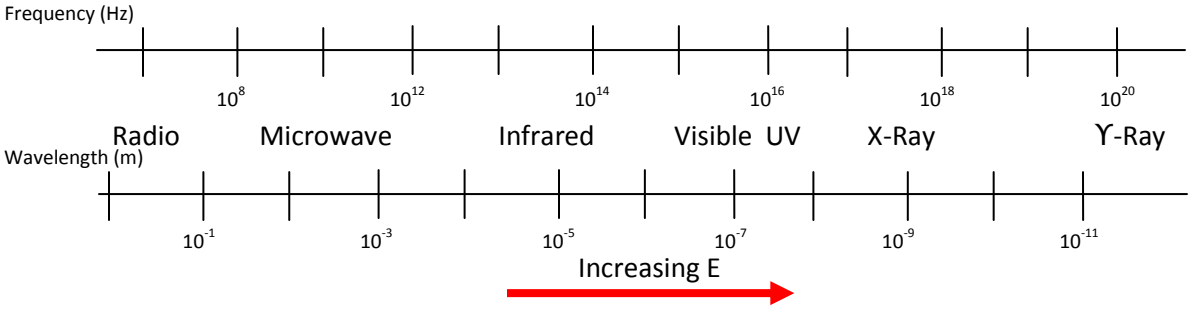


Figure 7. The electromagnetic spectrum with their corresponding frequencies and wavelengths

1.2.2 Vibrational Spectroscopy

Molecular vibrations occur whenever the atoms are in a periodic motion, and vibrational spectroscopy takes advantage of this form of motion. This spectroscopic method is especially useful to identify many of the physical properties of a molecule. In order for a molecular vibration to occur, a photon with energy exactly equal to the energy

of the vibrational transition must be absorbed. This absorption allows for the molecule to be promoted to an excited state. However, not every transition for the compound is possible, and each transition is governed by a set of selection rules, as is every spectroscopic method.

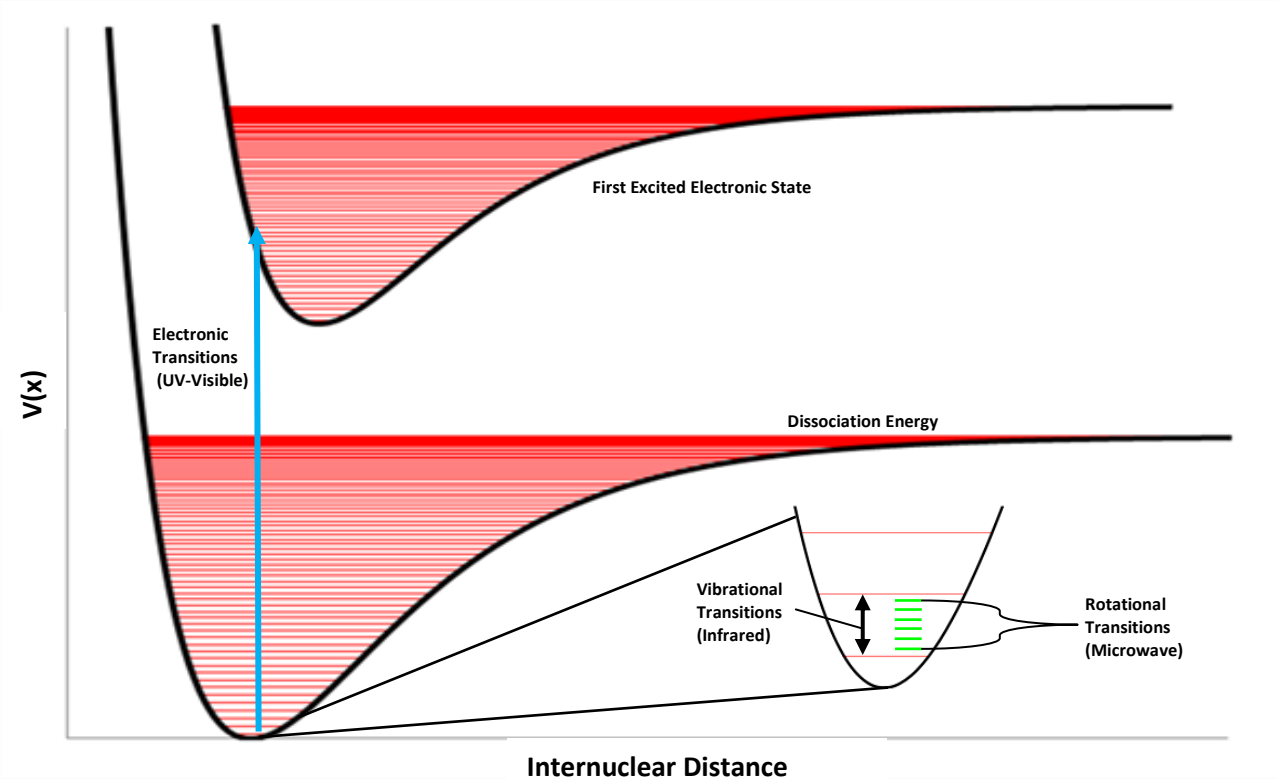


Figure 8. Major types of transitions that can occur and the corresponding region of the electromagnetic spectrum.

One reason Raman spectroscopy compliments IR spectroscopy so well is due to the two having separate selection rules. For a Raman band to be observed, there must be a change in the polarizability of the compound; whereas, IR spectroscopy requires there to be a change in the dipole moment for the observation of an IR active band.[110] Figure 8

shows some of the different types of transitions possible for compounds and the corresponding electromagnetic radiation needed to observe the transition.

To help in describing any changes that occur in the position of atoms in a molecule, the vibrational coordinates must be identified and help to describe the individual vibrations within a molecule. The word "normal" refers to two different normal modes being orthogonal (have an inner product of zero) in their displacement; moreover, the normal coordinates of an atom refer to the positions of said atoms compared to their equilibrium positions. To determine these normal coordinates, a determinate that includes the summation over the Cartesian coordinates of the positions of the atoms must be solved. It is well known that the number of normal modes of vibrations in a molecule possessing N atoms corresponds to 3N-6; whereas, a linear molecule possesses 3N-5 normal modes due to lack of observed rotation about the molecular axis. The number of normal modes is related to three degrees of freedom of motion (x, y, and z directions) for each of the atoms in the molecule minus the combined number of rotational and translational motions. Therefore, any observed motion of atoms in the molecule may be represented using an equation of motion that is a linear combination of the equations of motion for the normal modes. Each of these normal modes possess a particular energy associated with it.

1.2.3 Raman Spectroscopy

Raman spectroscopy allows for the study of molecular vibrations by studying the scattering of light. This was first discovered by C.V. Raman, who the process is named after.[111] As mentioned, since some vibrations are not IR active but Raman active and vice

versa, Raman spectroscopy compliments IR spectroscopy. For a vibration to be Raman active and, thus, seen in the spectrum, there must be a change in the polarizability of the molecule. A change in polarizability means that there is a distortion in the electron cloud around a vibrating atom.[109]

When an electromagnetic source is used to excite a sample, scattering by the molecules occurs for some of the radiation. When the light is scattered, there are three possible types of scattering. These are Rayleigh, Strokes, and anti-Stokes scattering and refer to the energy associated with the scattered photon.[109] When the energy of the photon is equal to the energy of the excitation source, the scattering is referred to as Rayliegh scattering which was named after the 19th century Lord Rayleigh. It is also known as elastic scattering because no energy is lost in the collision of the photons with the molecules.[112] If the scattered photon has less energy or more energy than the incident radiation, then Raman scattering has taken place. C.V. Raman was the first to observe these affects. Raman scattering occurs in a very small proportion of the scattered radiation; about 1 in a million photons are going to scatter with a different wavelength than the source. Anti-Stokes scattering refers to photons that have been scattered with more energy relative to the incident radiation; conversely, Stokes scattering occurs for photons that have been scattered with less energy than the incident radiation. Raman scattering occurs due to the inelastic collision of photons with the molecules in the sample causing the scattered photons to possess slight shifts in energy when compared to incident photons.[109]

When a photon possessing the energy hν interacts with a molecule, the molecule increases in energy by hν and is excited to a virtual state. This virtual state is not

quantized and can be thought of as an imaginary state between the first electronic state and the ground state. Upon relaxation from the virtual state a photon is scattered with either the same energy (Rayleigh scattering), more energy (Anti-Stokes scattering), or less energy (Stokes scattering) than the incident radiation.[109] This process is summarized below in Figure 9.

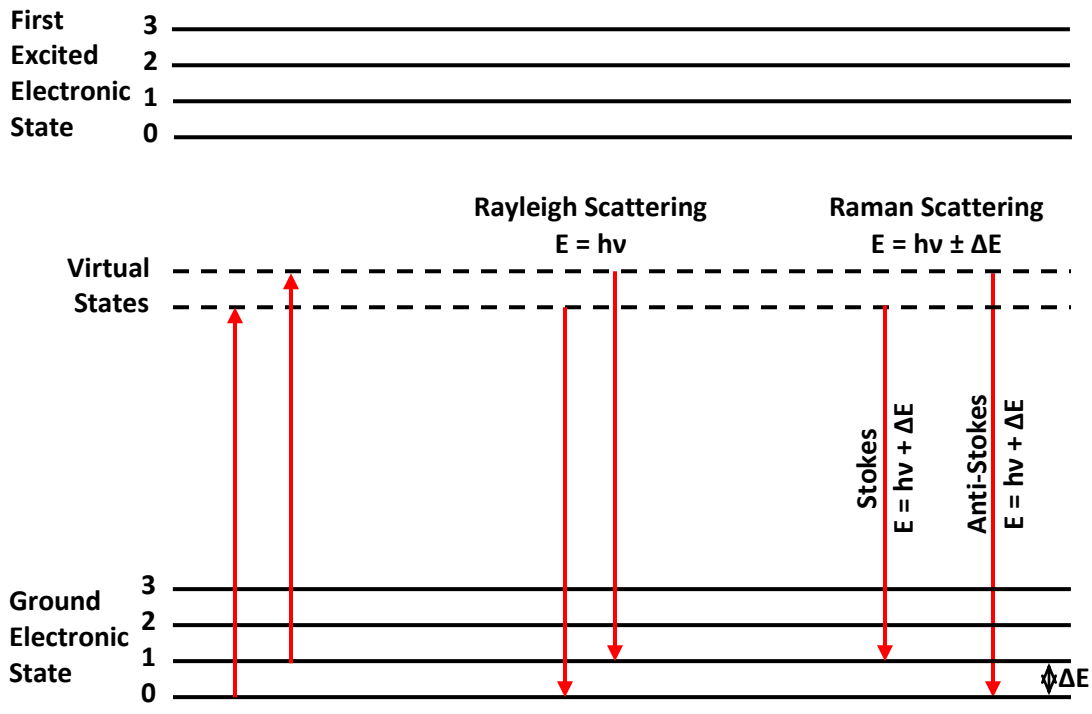


Figure 9. Diagram showing the main principles of Raman spectroscopy.

1.3 Computational Methods

Computational is a powerful and useful tool for chemists. However, the Schrödinger equation has proven to be unsolvable for systems that contain more than one electron (i.e. the hydrogen atom). Thus, to solve the Schrödinger equation, assumptions

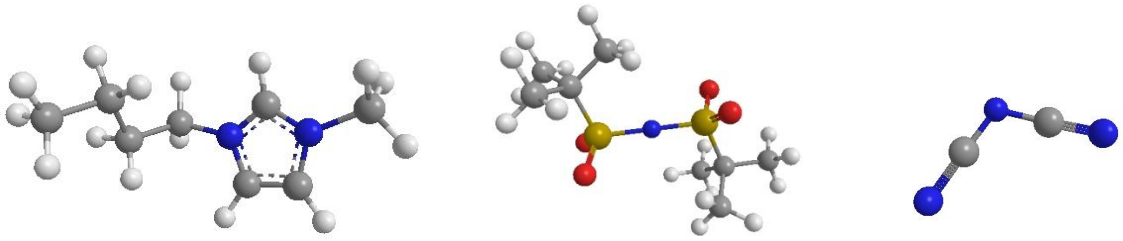
must be made to create a model of a system. With this in mind, these models are inherently inaccurate to some degree in describing real world systems; however, these models do provide a good basis for comparison with experimental data and usually yield a wealth of information. Furthermore, there are numerous models used to describe systems and computational chemistry is continuing to become more accurate in describing real world chemical systems.[110]

In this thesis, we utilized density functional theory for our computational calculations. It is now well-established that the B3-based DFT procedures provide a very cost-effective means of determining satisfactory harmonic vibrational transitions on a series of molecules in comparison with other procedures (B-based DFT or MP2 theory of perturbation).[113] There are various computational methods available to model chemical systems, but in this present paper, B3LYP density functional was mainly used to theoretically model the systems and allow for a comparison of the experimental data acquired. B3LYP was chosen because it has been shown to successfully model the anion/cation system of ILs in the literature.

2 Vibrational Spectroscopy of Ionic Liquids

2.1 Introduction

The goal of this thesis project has been to elucidate the complex interactions occurring between ionic liquids and hydrogen bonding donors, mainly methanol. It is our hope that this will help to clarify some of the concepts concerning ionic liquids and their study through vibrational spectroscopy. We focused on two main ionic liquids – 1-butyl-3-methylimidazolium bis(trifluoro-methanesulfonyl)imide (a hydrophobic RTIL) and 1-butyl-3-methylimidazolium dicyanamide (a hydrophilic RTIL).



(a) **(b)** **(c)**

Figure 10. The main ions studied in this paper. **(a)** shows the diagram for the cation 1-butyl-3-methylimidazolium; **(b)** shows the anion bis(trifluoro-methanesulfonyl)imide which was paired with the cation shown in (a); **(c)** shows the anion dicyanamide which was also paired with the cation shown in (a).

2.2 Experimental and Theoretical Methods

2.2.1 Spectroscopic Methods

The RTIL spectra were acquired using a Labview-controlled Jobin-Yvon Ramanor HG2-S Raman spectrometer. A double grating (2000 grooves/mm) monochromator and a photomultiplier tube detector were also employed in data collection. The 514.5 nm laser line of the Coherent Innova 200 Ar+ laser or the 647.1 nm output from a Kr+ laser was used as the Raman excitation source. The laser power measured approximately 0.5 – 2.0 W at the sample.

For micro-solvation of ionic liquids, samples were placed in a custom vacuum chamber and the solvent vapor was introduced onto the sample. The apparatus described is shown above in Figure 10. The RTIL samples were placed in a vacuum chamber to control the interactions that take place and to allow the micro-solvation of the RTILs by a hydrogen bonding donor.

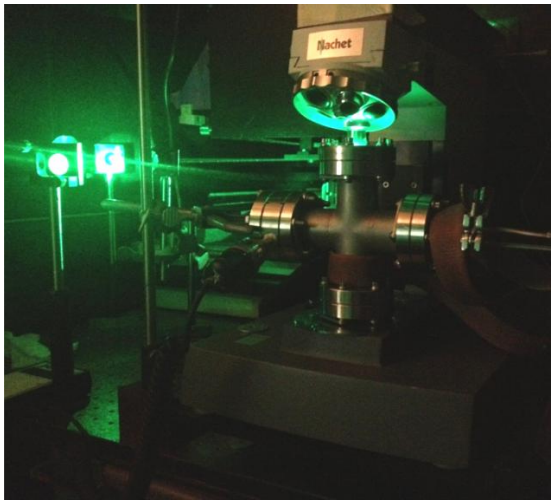


Figure 11. Aparatus for Micro-solvation of ILs designed by Kristina Cuellar.

2.2.2 Theoretical Methods

The Gaussian 09 software package was employed to optimize the structure and to calculate the corresponding Raman and infrared intensities. B3LYP density functional were used with a split-valence basis set 6-31G(d,p). A custom program developed with National Instruments LabView was utilized in the production of simulated spectra by combining Lorentzians for each normal mode.

2.3 Results

2.3.1 Spectroscopic Results

2.3.1.1 Neat Room Temperature Ionic Liquid Systems

The neat Raman spectra of bis(trifluoromethyl-sulfonyl)imide [C_4mim][NTf_2], of 1-(1-butyl)-1-methylpyrrolidinium bis(trifluoromethane-sulfonyl)imide [BMP][NTf_2] are shown in Figure 12 and Figure 13 respectively. The Raman spectrum of neat methanol provided by Kristina Cuellar can be seen in Figure 13. The Raman spectrum of 1-butyl-3-methylimidazolium dicyanamide [C_4mim][DCA] is shown in both Figures 14 and 15. In Figure 14, the spectrum was taken in atmosphere, and in Figure 15 the IL was exposed to vacuum for 36 hours prior to taking the spectrum.

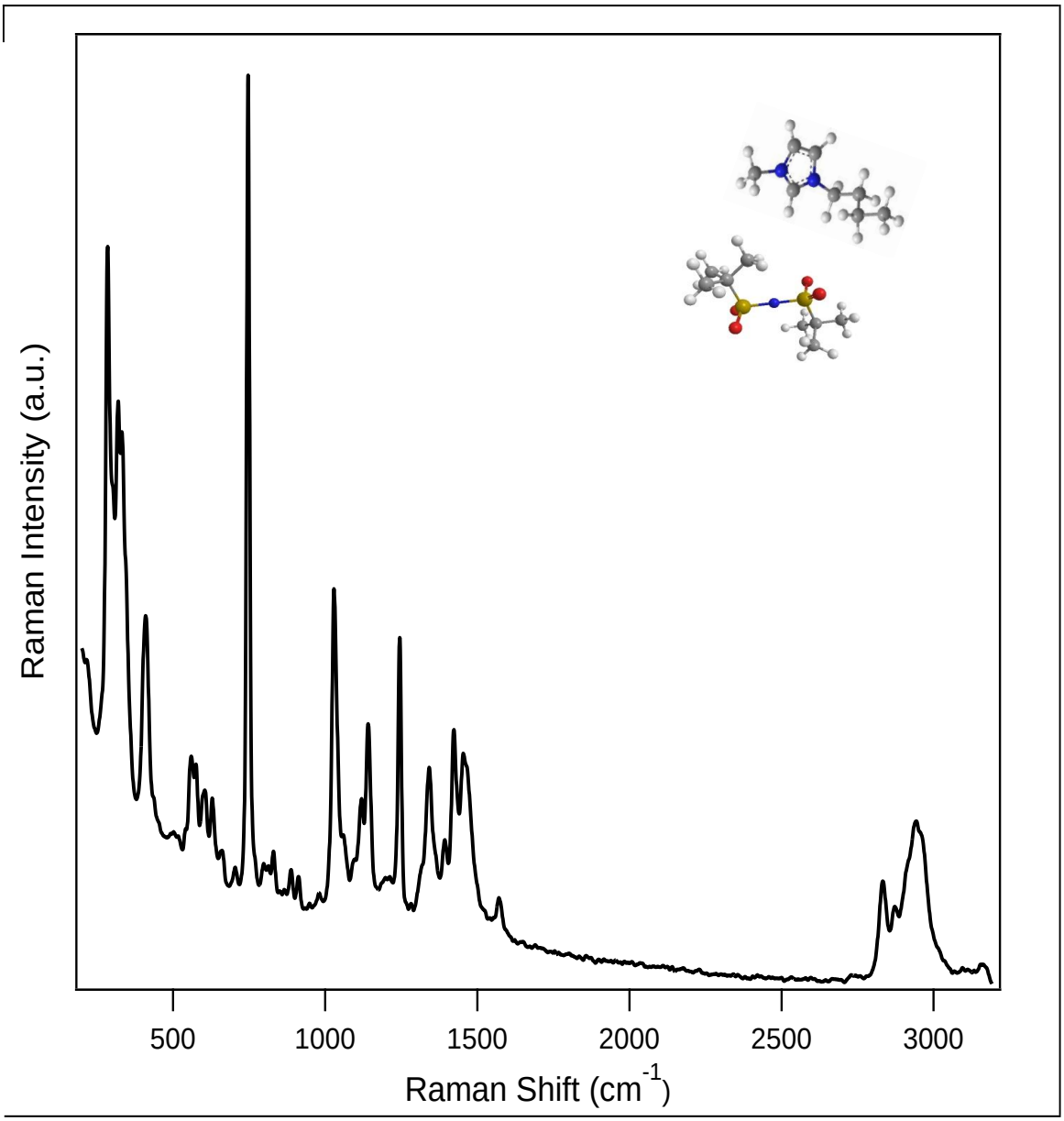


Figure 12. Shows the spectrum 1-butyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide [C_4mim][NTF_2] from 200 cm^{-1} to 3200 cm^{-1} using the 514.5 nm laser line with 2 watts of power.

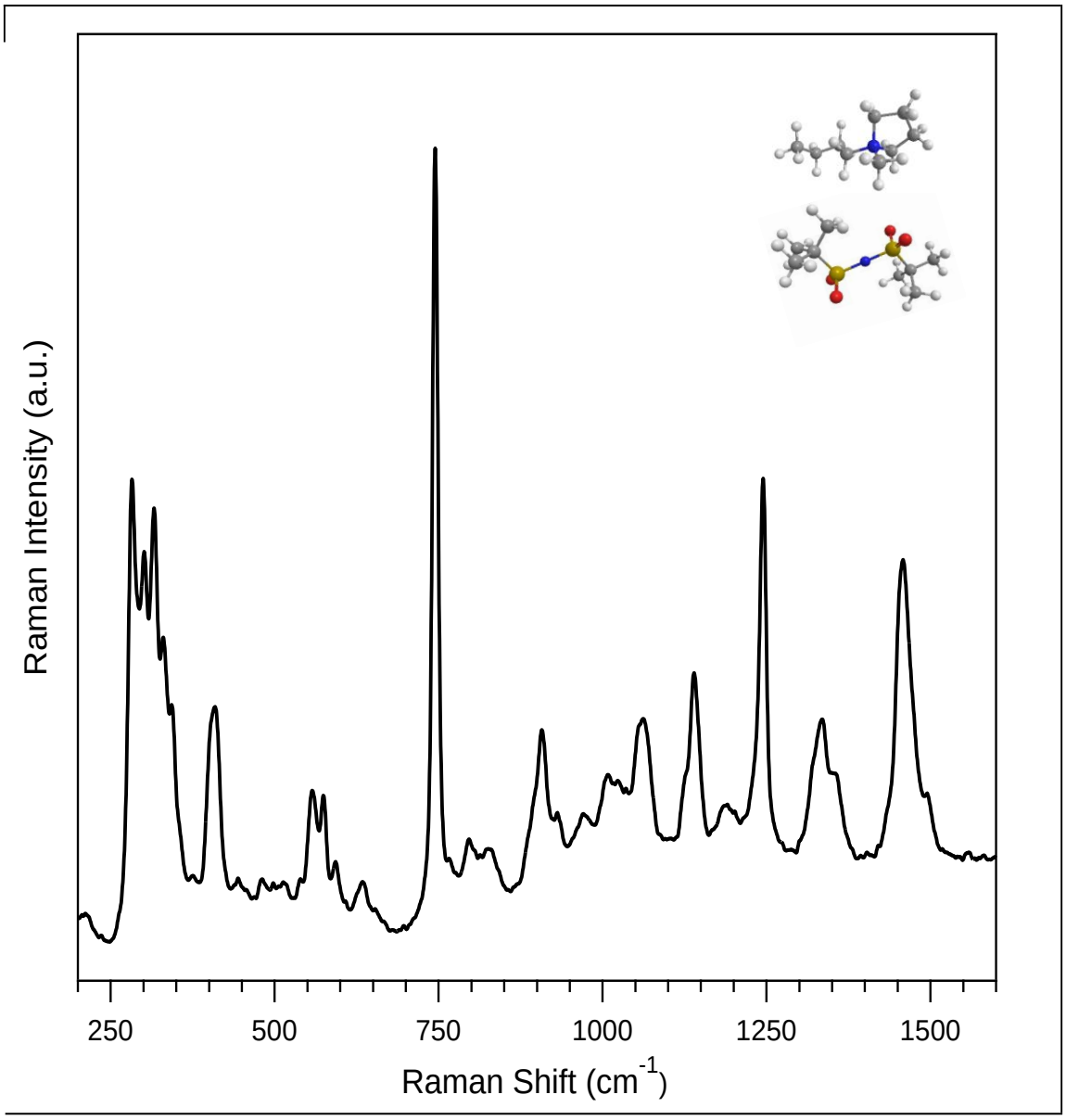


Figure 13. Spectra of 1-(1-butyl)-1-methylpyrrolidinium bis(trifluoromethane-sulfonyl)imide from 250 cm^{-1} to 1600 cm^{-1} with 2 watt laser power of the 514.5 nm laser line used.

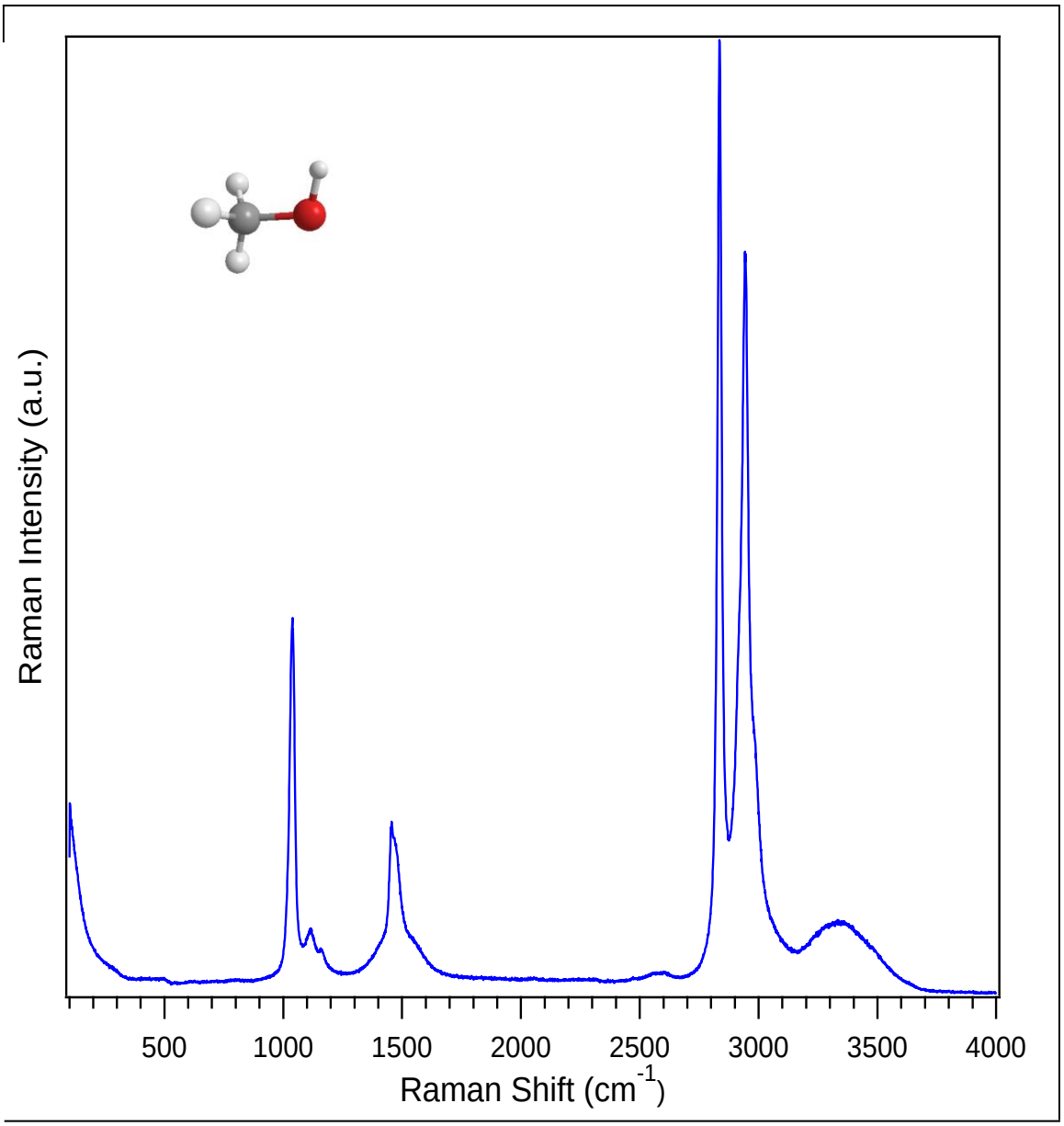


Figure 14. Methanol Raman spectrum taken and provided by Kristina Cuellar.

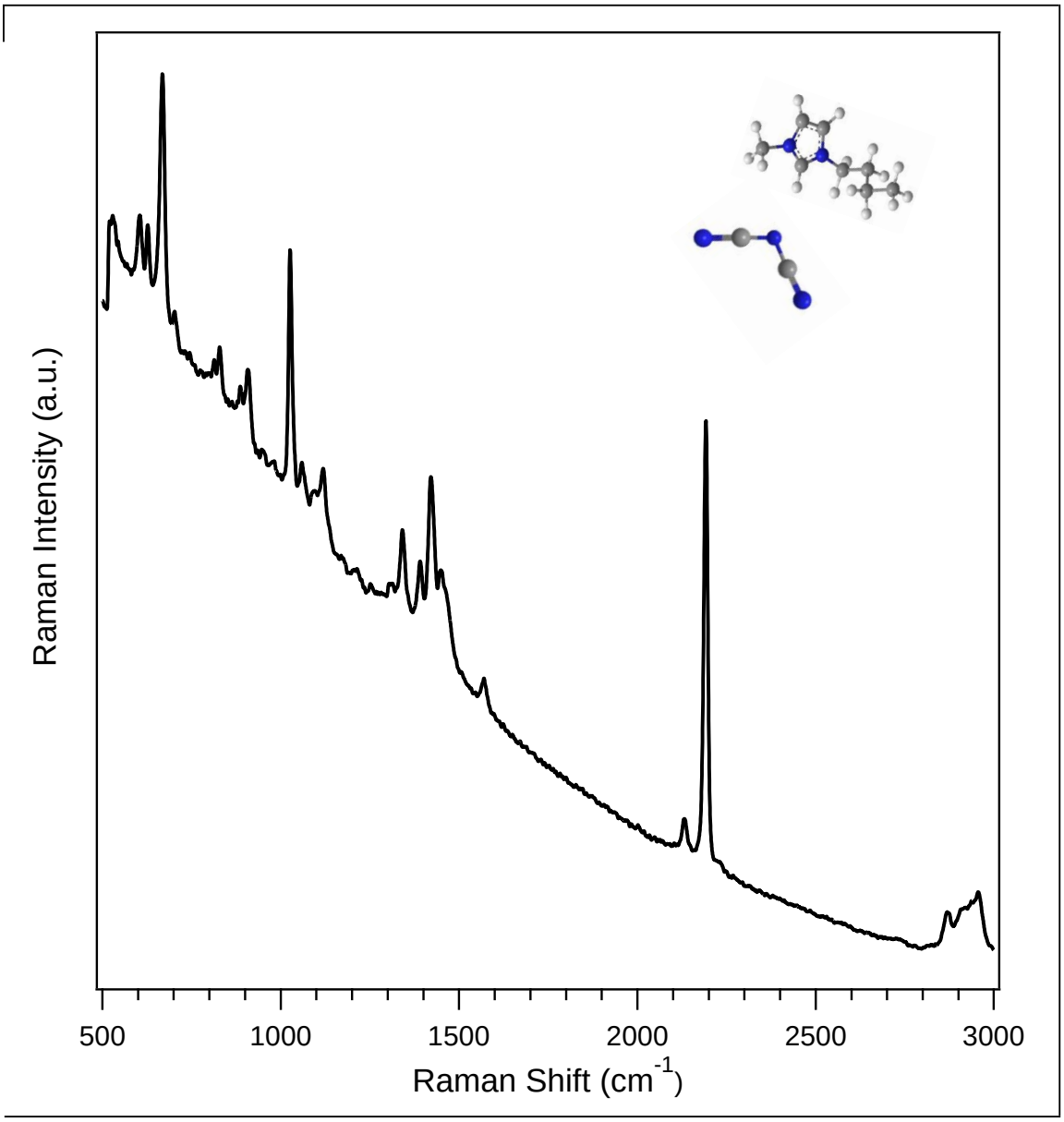


Figure 15. Raman Spectrum of 1-butyl-3-methylimidazolium dicyanamide using the 647.1 nm laser line.

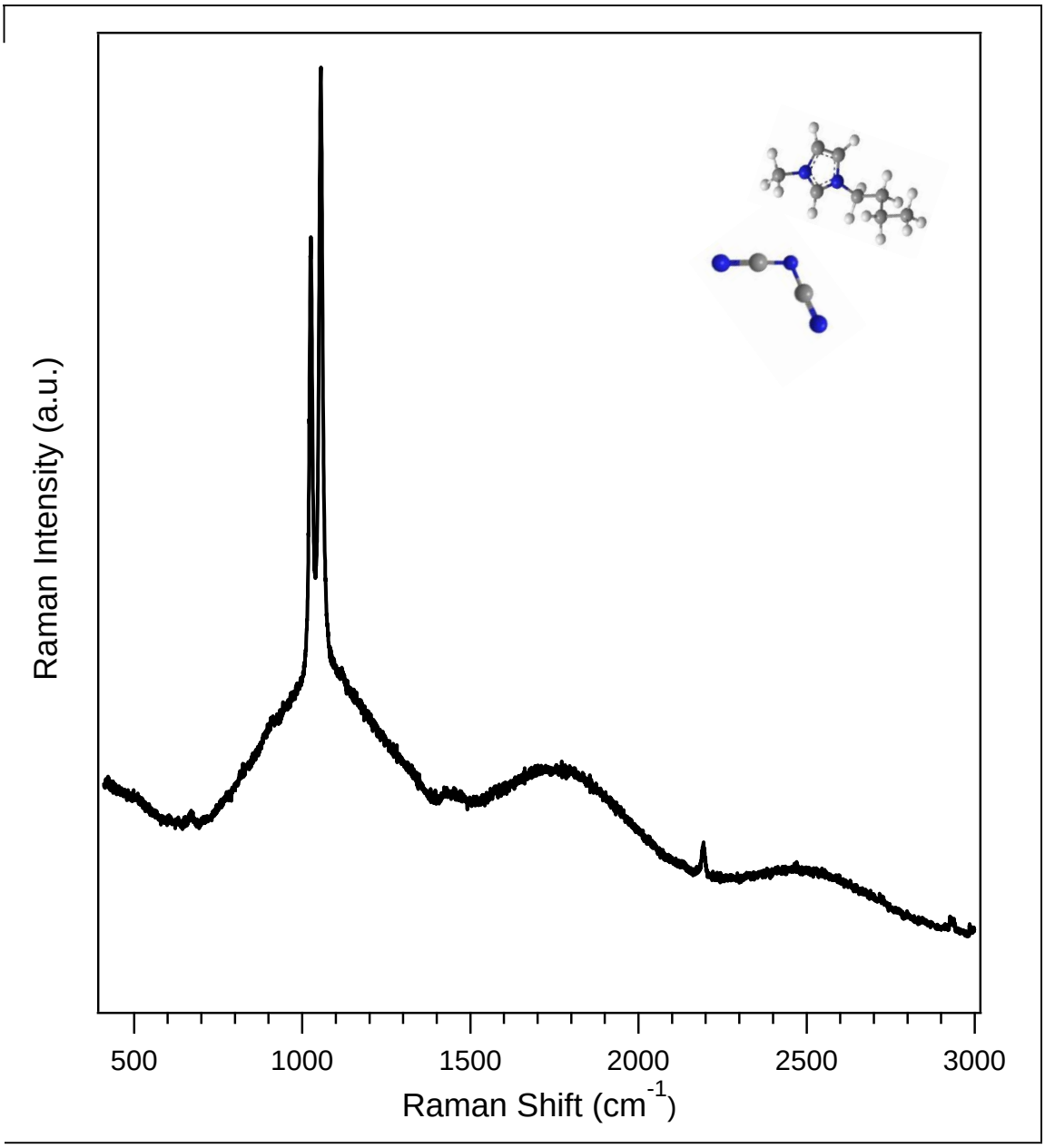


Figure 16. Raman Spectrum of 1-butyl-3-methylimidazolium dicyanamide under vacuum using the apparatus described earlier and the 647.1 nm laser line.

2.3.1.2 Ionic Liquid/Solvent Interactions

The spectra of 1-butyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide [C_4mim][NTF_2] and 1-butyl-3-methylimidazolium dicyanamide [C_4mim][DCA] with hydrogen bonding donors was further explored utilizing Raman spectroscopy. The micro-solvation with methanol of [C_4mim][NTF_2] is displayed in Figure 17 in the 200 to 1600 nm^{-1} range. A better comparison of the [C_4mim][NTF_2] and methanol is shown in Figure 18. A bulk mixture was also made of [C_4mim][NTF_2], and the Raman of this mixture is shown in Figure 19 in the range of 200 to 1600 nm^{-1} along with the neat IL and methanol spectra for a better comparison. This same comparison is shown in Figure 20 but from the range of 2700 to 3300 nm $^{-1}$. Figure 21 and Figure 22 show [C_4mim][NTF_2] micro-solvated with water from the ranges of 200 to 100 nm^{-1} and 1400 to 1600 nm^{-1} respectively.

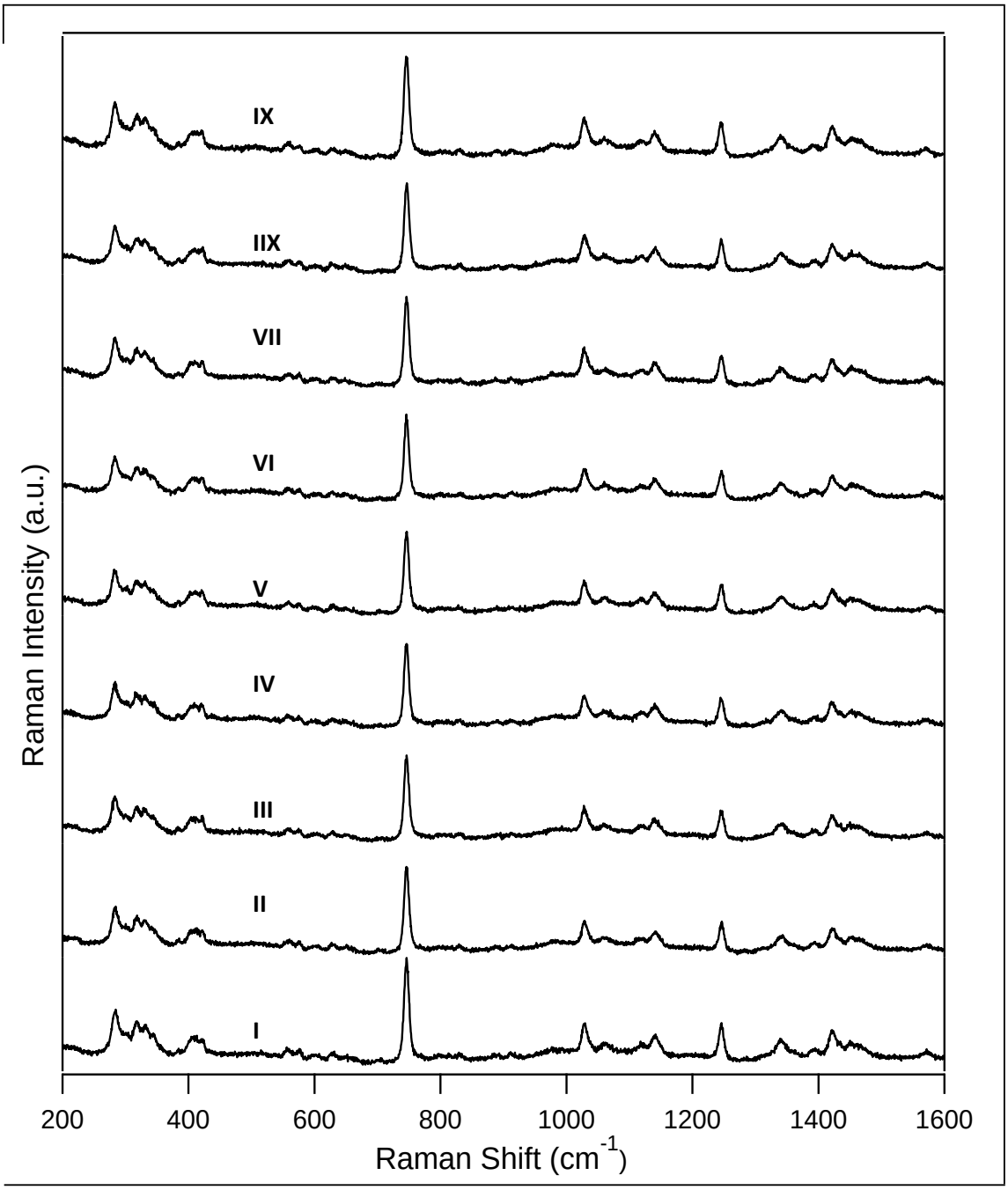


Figure 17. Micro-solvation of $[C_4mim][NTF_2]$ with methanol with additional heat applied to solvent source chamber. **(I)** shows the spectrum of the IL before micro-solvating with methanol. (II) 10 volts applied to heat source. (III) 20 volts applied to heat source. (IV) 30 V to heat source. (V) 40 V applied. (VI) 50 V applied to heat source. (VII) 60 V applied. (IIX) 70 V applied. (IX) 80 V applied.

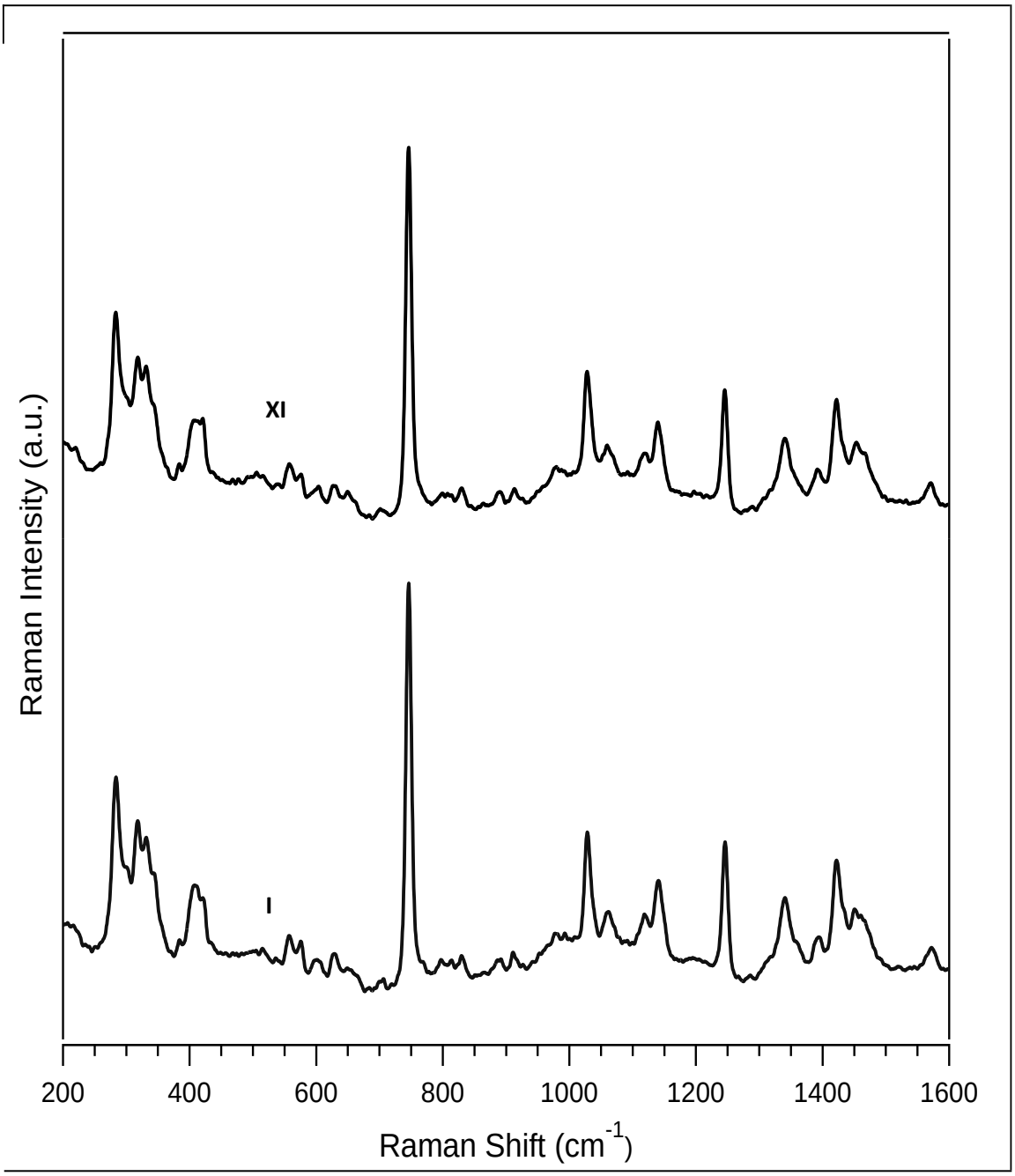


Figure 18. Shows figure 17(I) and 17(IX) for a better comparison of the effects of micro-solvation of $[C_4mim][NTF_2]$ with methanol.

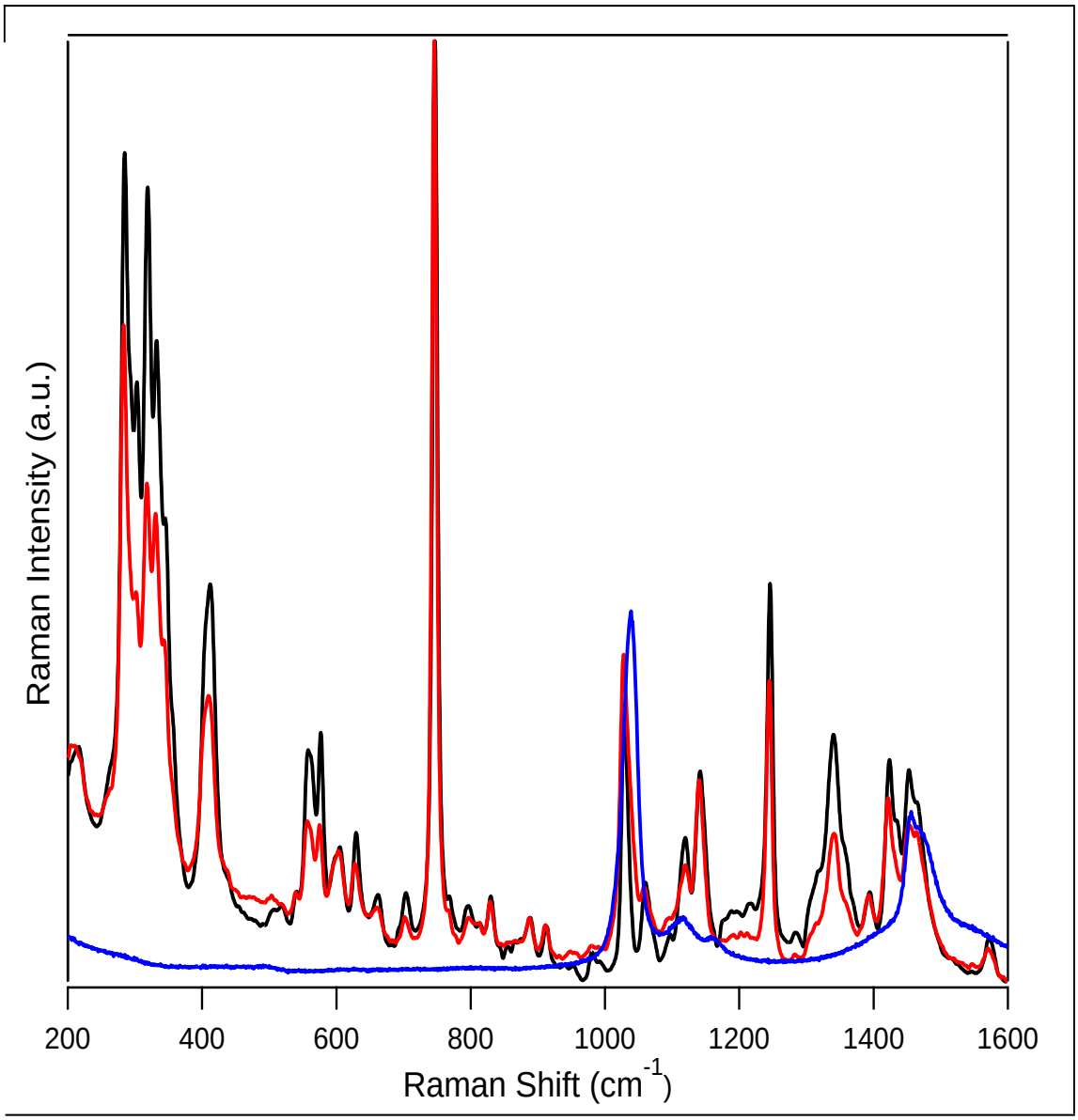


Figure 19. Shows the spectral comparison between 200 cm^{-1} to 1600 cm^{-1} between a neat methanol solution (blue line), the neat ionic liquid of $[C_4mim][NTF_2]$ (black line), and the $[C_4mim][NTF_2]$/methanol bulk solution (red line).

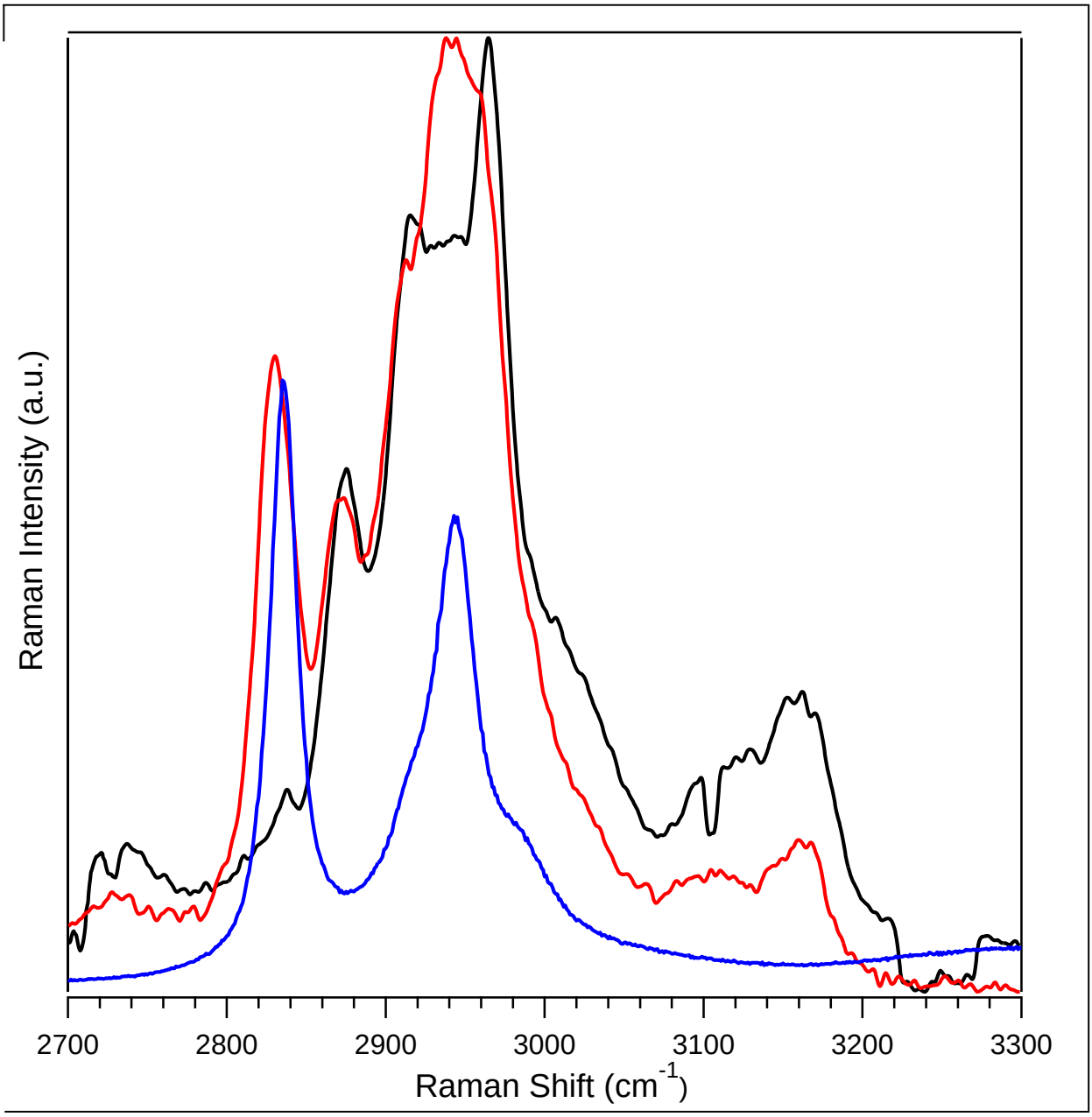


Figure 20. Shows the spectral comparison between 2700 cm^{-1} to 3300 cm^{-1} between a neat methanol solution (blue line), neat ionic liquid of $[C_4mim][NTF_2]$ system (black line), and an $[C_4mim][NTF_2]$/methanol bulk solution (red line). (The vibrational mode detected at approximately 3900 corresponds to a glitch in the Raman instrument while the data was being taken)

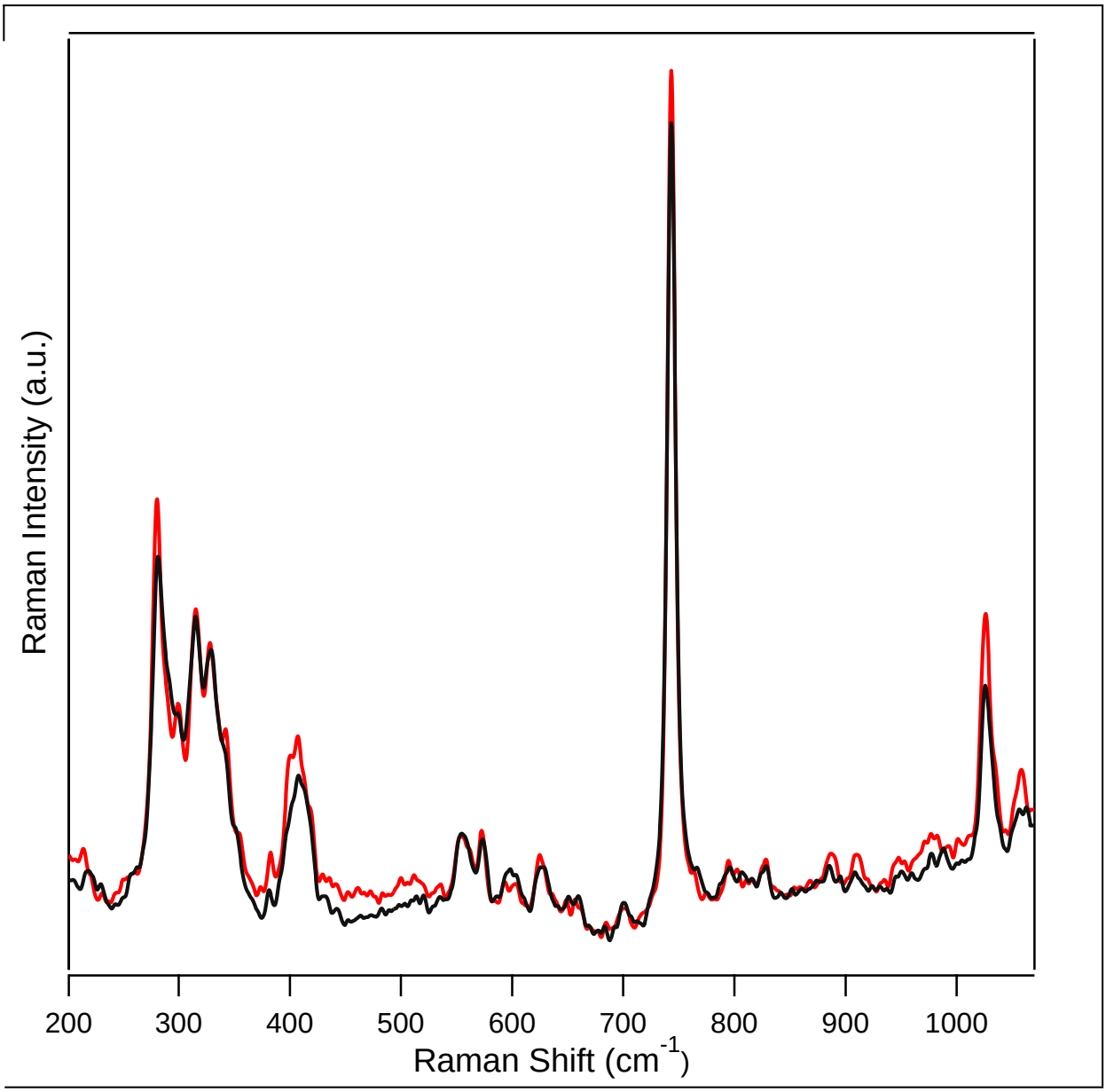


Figure 21. Spectrum of the micro-hydration of $[C_4mim][NTF_2]$ with water from 200 to 1100 cm^{-1} utilizing the 514.5 nm laser line.

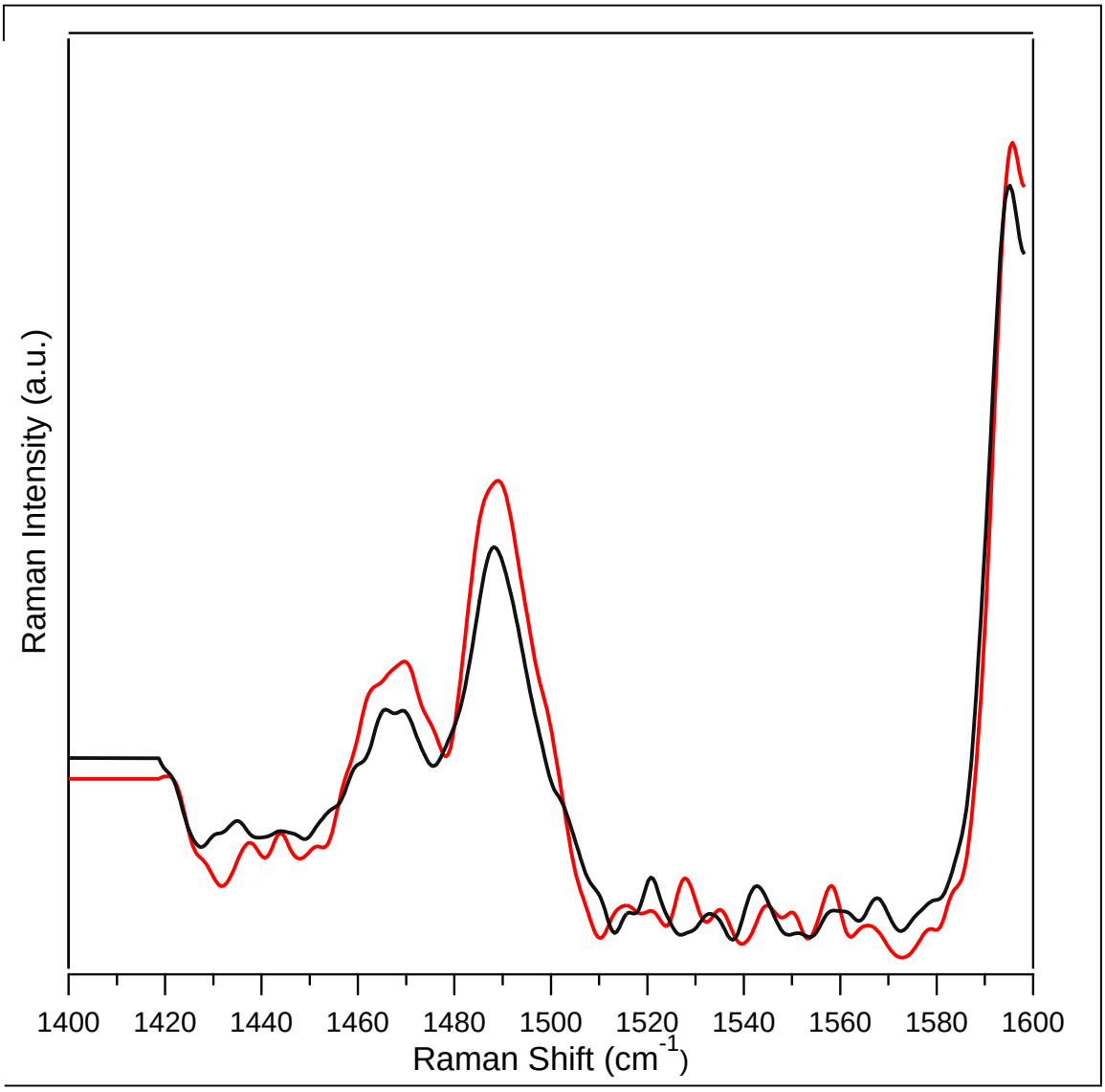


Figure 22. Spectrum of the micro-hydration of IL with water from 1400 to 1600 nm with the 514.5 nm laser line being used.

2.3.2 Theoretical Results

Figure 23 shows the optimized structure of 1-butyl-3-methylimidazolium dicyanamide using B3LYP/6-31g(d,p) level of theory. Figure 24 shows the theoretical Raman spectra obtained from the same level of theory. Figure 25 shows the comparison between the theoretical (red line) and experimental (black line) results.

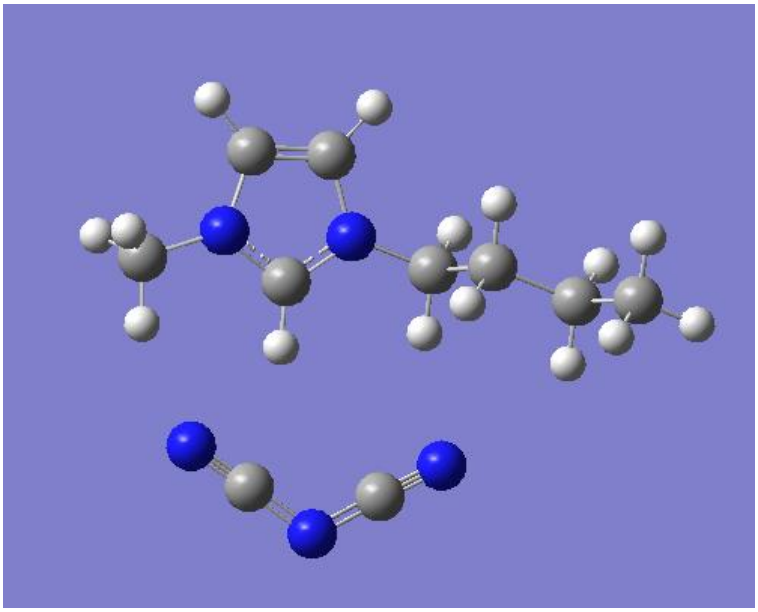


Figure 23. Optimized geometry of 1-butyl-3-methylimidazolium dicyanamide using the method B3lyp and the basis set 6-31g(d,p).

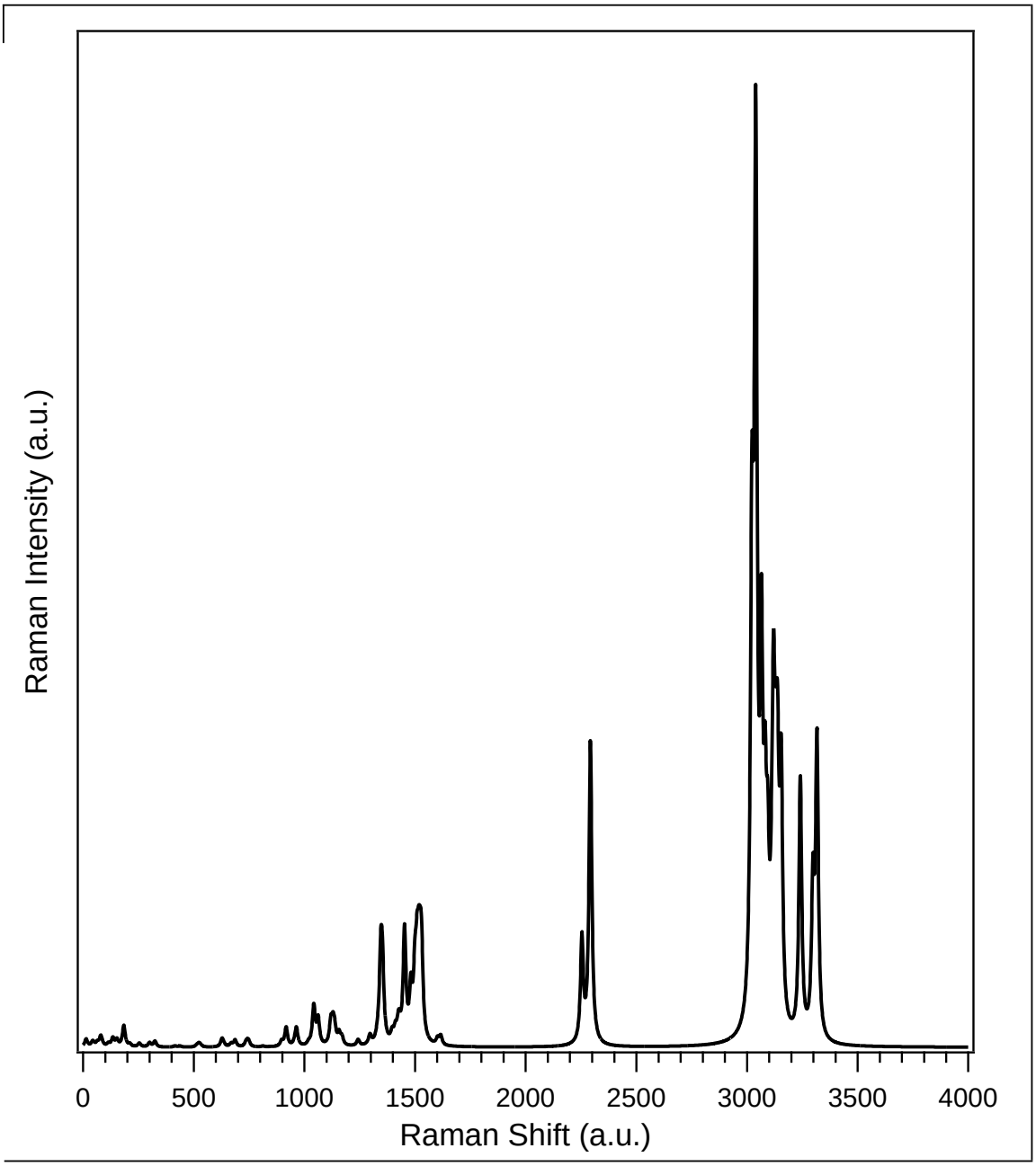


Figure 24. Theoretical Raman spectrum of 1-butyl-3-methylimidazoilium dicyanamide [C_4mim][DCM] using the B3lyp / 6-31g(d,p) level of theory.

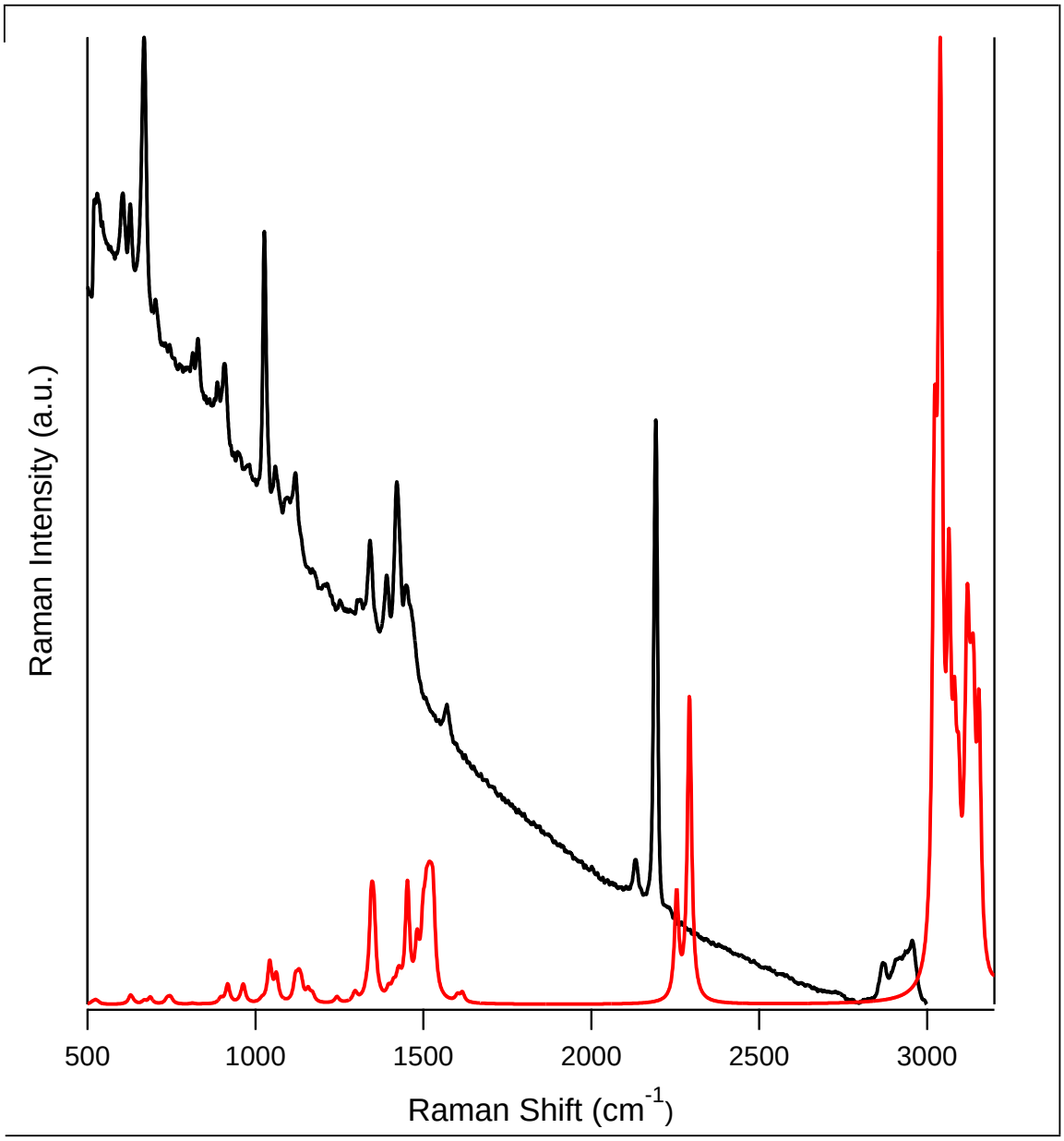


Figure 25. Comparison of the theoretical Raman spectrum of 1-butyl-3-methylimidazoilium dicyanamide [C_4mim][DCM] and of the experimental Raman taken in atmosphere.

2.4 Discussion

The neat IL spectra obtained agree nicely with reported literature spectra of ILs. Since many ILs are hygroscopic, the absorption of water from the atmosphere should be considered carefully when conducting any experimental procedures. As mentioned numerous times in the introduction, the addition of water or other organic solvent to the ionic liquid system can affect numerous physical properties of the liquids. It is these complex effects and interactions that we hoped to elucidate using the methods already described.

As can be seen with the spectra in Figures 17 and 18, few changes in the Raman spectrum were detected from the 200-1600 cm^{-1} range with utilizing our micro-hydration experiment. We had hoped that we would be able to detect red shifts or blue shifts within this region of the IL/solvent systems. However, looking closely around 400 cm^{-1} in Figure 18, we observe subtle changes in the two spectra. A closer comparison of this region is provided below in Figure 27 below. However, this change is not due to the addition of methanol as we had initially hoped but is due to the change in conformational equilibrium of the $[NTf_2]^-$ anion that results with the increase in temperature of the system as has already been described by Fujii et al.[88] A picture of the two conformations of the anion they reported can be found in Figure 26. Fujii et al. reported that the C_2 conformer was more stable than the C_1 conformer. Thus, the increase in the intensity observed with the micro-solvation experiment of methanol is due the increase in the presence of the C_1 conformer with increasing temperature.

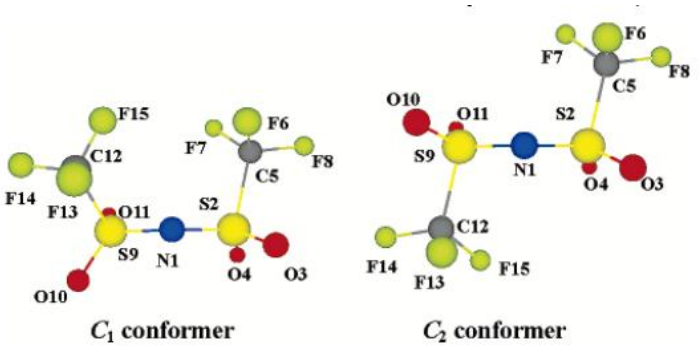


Figure 26. Different conformations for the $[NTf_2]^-$ anion taken from Fujii et al.[88]

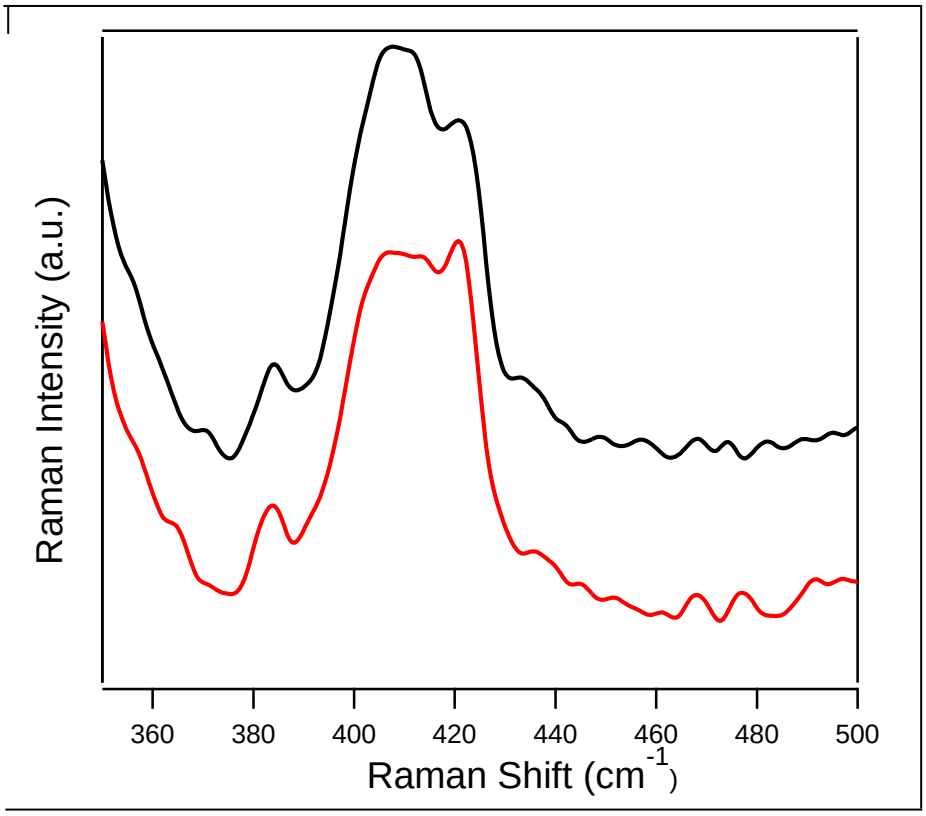


Figure 27. A better comparison of $[C_4mim][NTf_2]$. Red line shows the final spectra taken after the micro-solvation process with methanol. The black line displays the spectrum of the $[C_4mim][NTf_2]$ under vacuum. The difference in intensity as temperature changes is apparent and attributed to the differing stabilities of the anion conformations.

Looking at Figures 19 and 20, the bulk addition of methanol to the IL showed some subtle changes in the region of 2700 to 3300 cm^{-1} compared to the spectrum of $[C_4mim][NTf_2]$. However, these subtle change appear to be due to the methanol region of the spectrum as reported by Roth et al.[26] with $[C_2mim][NTf_2]$. It is difficult to look at the $[C_4mim][NTf_2]$/methanol spectrum and see changes in this region since both the C-H stretch from the imidazolium ring of the IL and the O-H stretching modes from the methanol both appear in this region. This is one reason why Roth et al. utilized deuterated methanol in their study. Therefore, the only way to get a better view of what is occurring in this area would be to utilize deuterated methanol in the solvent chamber of the micro-solvation apparatus. However, using deuterated methanol is currently not a practical step in the current experimental setup with the apparatus. Since bulk addition of methanol with this particular anion has already been accomplished by Roth et al., we decided to forego further experimentation until a better experimental setup could be provided to incorporate smaller amounts of deuterated methanol in the solvent source chamber. The micro-addition of water also gave a similar lack of appearant changes in the spectrum as can be seen in Figure 21 and Figure 22. Thus, we believed that our time might be better spent exploring a more hydrophilic IL that showed greater changes in the spectrum due to greater interactions between the IL and solvent.

The hydrophilic IL of 1-butyl-3-methylimidazolium dicyanamide $[C_4mim][DCA]$ was obtained from Dr. Hussey and constituted the rest of our experimentations. As can be seen Figure 15, the spectrum of $[C_4mim][DCA]$ exhibited a strong fluorescence background. This is an unfortunate occurrence in Raman spectroscopy; however, many of

the vibrational modes can still be observed. This spectrum was originally used as a preliminary data collection to insure that we could analyze this hydrophilic IL via Raman spectroscopy. Since we could see peaks in the spectrum, we decided to proceed by placing the sample in the vacuum apparatus described previously for 36 hours to assure all water from the sample was removed. After 36 hours, the spectrum was taken and is shown in Figure 16. This spectrum produced interesting features, with very strong intensity at a certain wavelength 1026 cm^{-1} and 1058 cm^{-1}. At first, we thought this might be due to a laser line not being properly filtered, but this was soon rejected after a few calculations. This peak is currently still being identified but may be due to a chemical change that occurred while the IL was in vacuum or a problem with the experimental setup of the apparatus.

All of the theoretical calculations done (Figures , were done to help explain the potential experimental results obtained from [C_4mim][DCA]; however, since we encountered trouble with this IL in vacuum, we decided to forego further experimental and theoretical calculations until the problem was resolved. Thus, we were unable to attempt any experimentation by micro-solvation with the RTIL of [C_4mim][DCA] due to the complications that were encountered during the data collection. We are still hopeful that we can resolve the problems encountered with this RTIL or perhaps proceed to experiment with another hydrophilic RTIL.

2.5 Conclusion

While many systems we've studied in our lab have readily shown changes in the spectra on addition of a hydrogen bonding donor, the RTIL and solvent systems (at least the ones studied here) appear to exhibit a number of experimental complications associated with these unique systems. A more thorough investigation of the literature to find RTILs that are hydrophilic and exhibit no fluorescent impurities is essential to future studies of this nature, but we are hopeful that either other RTILs may not exhibit the same problems encountered here or that we can overcome the experimental problems described in this thesis. ILs represent a unique and fascinating system to study both experimentally and theoretically and are only going to continue to find applications in industry and academia.

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