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A Raman Spectroscopic Study of the Effects of Hydrogen Bonding on 1,2,3-Triazole

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A RAMAN SPECTROSCOPIC STUDY
OF THE EFFECTS OF HYDROGEN BONDING
ON 1,2,3-TRIAZOLE

By: Anna Elizabeth Craig

A thesis submitted to the faculty of the University of Mississippi in partial fulfillment of the requirements of the Sally Barksdale Honors College.

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Dedication

This thesis is dedicated to Ada Mariel Vivieca Franco, Happyness Elias Messana, Karla Carolina Mineros Roque, Josue Elias Augilar Argueta, Weerayut Janmontree, and Ismael Perez. I've had the pleasure of getting to know each of these children through Compassion International and pray that they, too, will have the opportunity to pursue an education. Foremost, I pray that they will realize the blessing they have been in my life, and that they will persevere through all trials in life, leaning on God and growing continually in their faith.

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ABSTRACT

ANNA ELIZABETH CRAIG: A Raman Spectroscopic Study of the Effects of

Hydrogen Bonding on 1,2,3-Triazole

(Under the direction of Dr. Nathan Hammer)

The goal of this thesis is to analyze the effects of hydrogen bonding on liquid 1H-1,2,3-triazole. Spectra of neat 1H-1,2,3-triazole are compared to simulated spectra and are found to differ greatly. The experimental spectrum, however, matches the simulated spectra of 1H-1,2,3-triazole dimers very well. This suggests that dimers play a large role in the liquid structure of 1H-1,2,3-triazole. Though tautomerism is thought to play a large role in the vibrational behavior of 1,2,3-triazole, the Raman spectra obtained here suggest that molecular dimers dominate the liquid state much more so than tautomerism. Even in aqueous solution, the simulated spectra of dimers hydrogen bonded with water networks match the experimental data very well.

Table of Contents

List of Figures

1 Introduction

1.1 Triazoles

Triazoles have numerous uses in today's world, including applications in medicine and explosives, and there is currently much interest in the study of triazoles.[1] A triazole is a five membered cyclical ring consisting of three nitrogen atoms, two carbon atoms, and three hydrogen atoms. Figure 1 shows the molecular structure of 1H-1,2,3-triazole. An important feature of 1,2,3-triazole is that the hydrogen can move from the 1H position to form 2H-1,2,3-triazole in solution in a process called tautomerism. Currently there is much debate as to the form of 1,2,3-triazole in different phases and solutions.
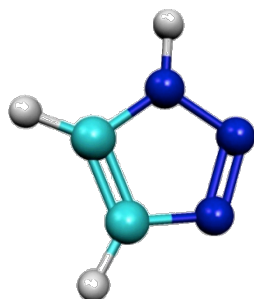
Figure 1: Molecular model of 1H-1,2,3-triazole.

Triazoles have been found to be particularly useful in pharmaceutics as they make up the vital components of many medicines, such as Fluconazole and Tazobactam.[2] Their derivatives are capable of tackling numerous types of diseases including fungus based infections and some bacterial infections. Triazoles possess anti-inflammatory and anti-microbial properties which allow them to work well as antibacterial agents.[3] Advances and new developments in pharmaceutics are in high demand because bacteria often build up resistance to certain medications. In 2001, an evaluation was done by A.R. Bhat on triazoles

as a medication for tuberculosis, and it established them to have anti-tubercular properties.[4]   Some common medications containing triazoles as molecular building blocks are Albaconazole, Fluconazole, Itraconazole, Posaconazole, Terconazole, and Voriconazole. All of these medications come in the form as anti-fungal creams. They work by keeping ergosterol from being produced. This process causes methylsterols to build up, which in turn causes the death of fungus and ceases its growth.

1,2,3-triazole is used in the medication Tazobactam, which inhibits the action of bacterial beta-lactamases. It is used as treatment for community-acquired pneumonia.[5] Mark Sanford studied the use of Anastrozole, a triazole derived medication, in postmenopausal women as treatment for breast cancer. He compared Anastrozole to the use of Tamoxifen, and found that when breast cancer was treated with Anastrozole, the survival rate of the women was higher.[6] In 2013, 1,2,3-triazole was suggested to be an excellent anti-vemon for viper bites and is used in the treatment of schizophrenia as well.[7] Triazoles are remarkably versatile and functional in the field of medicine.

The uses of triazoles are not bound to the medical field however; they span into a broad variety of areas. Their various derivatives can be powerful corrosion inhibitors, particularly benzotriazole.[8] Triazoles are also beneficial for plant life in that they can be used as herbicides and fungicides.[9] The agricultural industry benefits greatly from the increase in crops that occurs when a triazole is used as an herbicide. In her article in the *Farmer's Weekly Journal*, Julian Gairdner urges farmers to use triazole herbicides on their beets to get a five percent increase in their crop yield.[10] However, similar to antibiotics, triazole

cannot be used excessively, as resistant strains to the triazole will transpire, and the triazole will be less effective as a treatment for plant disease. Syngenta, a leader in world agriculture, recommends farmers to use a maximum of two sprays of triazole on their crops, with one spray being sufficient. This will guard the efficiency of triazoles as herbicides in the future.[11]

Another characteristic of triazoles is that, because of their high ring strain and high energy, they work well as explosives. They can also be used as an alternative for polymer membrane electrolyte fuel cells (PEMFCs). Research scientists at Georgia Tech claim that the use of triazoles in PEMFCs will reduce the cost of manufacturing and also increase efficiency. This is because triazoles will enable PEMFCs to operate at "higher temperatures without moisture."[12] Because a triazole molecule has three nitrogen atoms, it can be expected to be quite energy rich; in other words, triazoles house a large amount of energy within their frame. According to Alexander Goncharov of the Carnegee Institution for Science, "'Nitrogen compounds tend to be high energy density materials.'"[13] This is very valuable to the military, especially because triazoles are much more "green" than previously used explosives such as TNT.[14] In fact, 1,2,3-triazole is "considered to be one of the most promising backbones for the fabrication of high performance explosives because they possess relatively high heats of formation."[15] Triazoles and their various applications should be studied further to discover more advantageous properties and the reasons behind those properties.

The hydrogen bond between 1,2,3-triazole molecules, especially in the crystalline phase, is known to be very strong and amongst the strongest observed

for NH-N systems.[16] Such interactions are likely to also exist in the liquid phase and in 1,2,3-triazole solutions as well and affect their chemical properties. The focus of this Honors Thesis is to use Raman spectroscopy and quantum chemistry to explore the competition for hydrogen bonding between 1,2,3-triazole molecules and between 1,2,3-triazole and water when hydrated.

1.2 Noncovalent Interactions

Noncovalent interactions are important in virtually all areas of chemistry.[17] Such interactions do not involve the sharing of electrons like covalent bonding, and, as a result, are weaker. There are several types of noncovalent bonds: van der Waals interactions, hydrophobic bonds, ionic bonds and hydrogen bonds.[17] Van der Waals interactions occur in all molecules and result from the transient induced dipole within the molecule. This happens when, as the electrons in the molecule are moving, one area contains more electrons that another, making one area more positive and the other more negative. This is not a permanent dipole and, as a result, forms very weak bonds. As distance between the molecules increase, the strength of the van der Waals interactions declines. On the other hand, if the molecules get too close to each other they will be repelled.

Hydrocarbon-based molecules have hydrophobic interactions. Because hydrocarbons are not soluble in water, water forms a network of hydrogen bonds around the molecule but not with it. This decreases the randomness of the water molecules, and thus costs energy because of the distortion of the water molecules.[18]

Essentially, hydrophobic bonds demonstrate how nonpolar substances only dissolve in nonpolar substances, while polar substances only dissolve in polar substances.

Ionic bonding is the bonding of two atoms that have opposite electrical charges; it involves a cationic species and an anionic species.[17]   No sharing of electrons occurs in ionic bonding. Instead, the molecules are attracted to each other because of their opposite charges. There is no specific orientation to the bond because "the electrostatic field is uniform in all directions.[19]

The focus of this thesis is on the hydrogen bonding of 1,2,3-triazole with itself and with water. Hydrogen bonding is well described by its name; it involves hydrogen as well as another atom. That other atom is most always oxygen or nitrogen. This bonding occurs because the electronegative atom, such as oxygen or nitrogen, carries a partial negative charge, while the hydrogen will carry a partial positive charge. This makes oxygen or nitrogen on other molecules attracted to the hydrogen and a bond will form. Hydrogen bonding is relatively strong compared to other noncovalent bonds. It is approximately one tenth as strong as a covalent bond.[20] Though not very strong in comparison to a covalent bond, these bonds are powerful enough to give water its many, distinct characteristics, as well as cause shifts in the Raman spectra of the triazole molecules examined in this study.[21]

A hydrogen bond can be intramolecular, intermolecular, or a pi system hydrogen bond. An intramolecular hydrogen bond occurs inside a single molecule. In other words, the molecule is hydrogen bonding with itself. For this to occur, the molecule must have a hydrogen donor and a hydrogen acceptor within reach of each other. On the other hand, an intermolecular hydrogen bond arises between

two different molecules. The molecule can react with any other molecule that is capable of hydrogen bonding; they do not have to be the same. The hydrogen donor and acceptor both must be in place to bond however. In a pi system hydrogen bond, a set of pi electrons from an aromatic ring bonds to a hydrogen.[22]

Both strong and weak hydrogen bonds exist in nature. A strong hydrogen bond is one that involves the typical electronegative atom such as oxygen or nitrogen. A weak hydrogen bond, on the other hand, would be a case in which the hydrogen attached to a carbon (or any other non-nitrogen/non-oxygen atom) interacts with the oxygen from water. This type of hydrogen bond is weaker because the hydrogen atom that is attached to a carbon atom will not have as much of a partial positive charge as a hydrogen atom that is attached to a nitrogen atom.[23] An example of both strong and weak hydrogen bonding is presented in Figure 2. The more electronegative nitrogen atom (blue) or oxygen atom (red) is more capable of pulling the negative charge toward itself, whereas a carbon atom (teal) will not hoard the electrons in the same way because of its weaker electronegativity. This leaves the hydrogen atom more neutral in comparison to a hydrogen atom involved in a strong hydrogen bond; therefore, it is less apt to react with a negative oxygen or nitrogen atom.
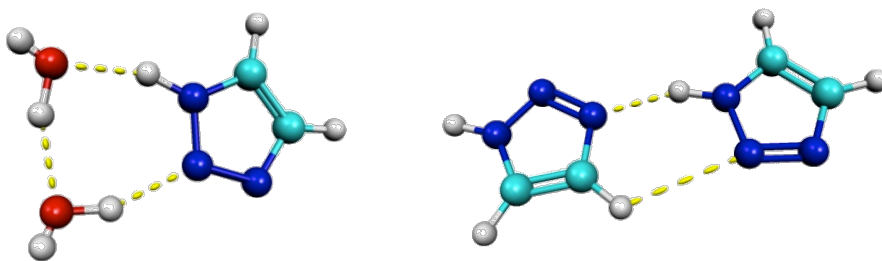

Figure 2: An example of strong NH···O and OH···N hydrogen bonds (left) and strong NH···N and weak CH···N hydrogen bonds (right).

Hydrogen bonding is affected by the electronegativity and size of the atoms involved. For example, water molecules are capable of hydrogen bonding with one another, but hydrocarbons are not. This is because, in water, oxygen is bonding with the hydrogen. Oxygen is a very electronegative atom, especially compared to hydrogen, so when an oxygen atom bonds to a hydrogen atom, the oxygen atom will have a partial negative charge because the electrons will be drawn more so to oxygen atom than the hydrogen atom. This will leave hydrogen atom with a partial positive charge. Opposite charges attract, so the hydrogen atom is more attracted to the oxygen atom, and the oxygen atom is likewise drawn to the hydrogen atom. A hydrogen bond has been formed. On the other hand, carbon is not very electronegative and neither is hydrogen. So, when a hydrogen atom and a carbon atom bond, the electrons are not any more likely to side closer to carbon atom than they are to hydrogen atom. This situation illustrates a more equal sharing of electrons, which is definitely not the case in hydrogen bonding. Consequently, a hydrogen bond is not created.[23]

The size of each atom is important as well. When an atom has a large electron cloud, the nucleus, holding the positive charge, will have a difficult time participating in the interaction. Smaller atoms are able to have strong bonds much easier because their nucleus is not as far from the outer edge of the electron cloud. A large atom has a large radius which makes it difficult for the nuclei to contribute to the interaction.[23] So, smaller atoms will have a greater ability to form hydrogen bonds compared to larger atoms.

1.3 Tautomerism of Triazoles

1H-1,2,3-triazole is capable of tautomerizing from the 1H form to the 2H form and vice-versa. In the 1H form, the hydrogen is attached to the first nitrogen atom. In the 2H, it is on the second nitrogen atom. Although there has been much controversy in this area, 2H-1,2,3-triazole is thought to be the predominant tautomer in the gas phase, while both 1H and 2H exist in solution.[24] For example, in 2013 Oziminski reported that the 2H form is the most abundant in gas phase. However, in solution the 2H form is reduced because hydrogen bonds interfere with the -effect. The -effect is the "repulsion of lone pairs belonging to two adjacent nitrogen atoms and only affects the 1H tautomer."[25] Begtrup's computations suggested the ratio of 1H to 2H to be 1:1000 in gas phase.[26] On the other hand, Borello's vibrational spectra suggested that the 1H tautomer was most prevalent in gas phase.[27] Albert and Taylor found that in water, the ratio of 1H to 2H is 1:2.[28] The consensus on the difference in prevalence of each tautomer in the various phases is that the "tautomerization energy is decreased by a polar solvent because of the hydrogen bonds lowering the -effect."[25] The solid phase has been studied as well. Goddart performed single crystal X-ray diffraction and suggested that there is a 1:1 ratio of 1H to 2H-1,2,3-triazole in the solid phase.[29]

Studies of 1,2,3-triazole tautomerism has been done in several types of solution. Lunazzi observed a 0.5 M solution of 1,2,3-triazole and chloroform with HNMR at room temperature and found that the 2H tautomer made up 80% of it. He then used a 0.01 M solution of triazole in tolune and found a 1:4 ratio of 1H to 2H tautomers. However, when he used the same mole ratio or 0.01 M triazole

and chloroform the ratio was reversed. The difference in ratio he claimed to be because the polar chloroform and nonpolar toluene. So, the 2H tautomer was more present in a nonpolar solvent, and the 1H tautomer was more present in the polar solvent.[30]

Tautomerism of 1,2,3-triazole in the liquid state has been much less studied. A very recent report investigating tautomerism of liquid 1,2,3-triazole using energy-dispersive x-ray diffraction and Fourier transform infrared spectroscopy (FTIR) suggested that a mixture of both tautomers exists in the liquid state.[31] Here we investigate this phenomenon using Raman spectroscopy and quantum chemistry calculations.

1.4 Vibrational Spectroscopy

According to the Merrium-Webster dictionary, spectroscopy is defined as the "study of the absorption and emission of light and other radiation by matter, as related to the dependence of these processes on the wavelength of the radiation."[32] Vibrational spectroscopy includes both Raman and infrared absorption (IR) spectroscopies. Through these methods, information about the structure of the molecule, interactions, as well as composition can be discovered because each molecule has its own "fingerprint." In other words, the vibrational energy levels for each molecule or substance are different, making it a convenient method for differentiating one molecule from another.[33] The information gathered by the instrument will be presented in the form of a spectrum. In IR spectra, the plot is the amount of light absorbed or transmitted verses the energy.

Raman spectra, on the other hand, show intensity of Raman scattered light verses frequency, usually in wavenumbers.[34]

According to Dr. Henry Ellis, "Vibrational energy is the kinetic energy associated with relative motion of atoms which constitute the molecule."[35]   In other words, it is simply the stretching and contracting about the axis of inertia at the equilibrium distance.   The model that vibrations follow is the harmonic oscillator model.

1.5 Raman Spectroscopy

Both elastic and inelastic scattering occur when light strikes a molecule. Elastic scattering is referred to as Rayleigh scattering. This is the most prevalent scattering that occurs; however, there is no difference in the energy between the excited and emitted photon. It is therefore not used in the spectroscopic techniques employed in this study. On the contrary, the inelastic scattering, also known as Raman scattering, is helpful because it displays a difference in energy. In the case of Raman spectroscopy, energy is either lost or gained within the molecule when monochromatic light from a laser interacts with it. A high powered source of light is necessary because the Raman Effect is not very strong. In fact, only one out of every million scattered particles has a measureable change in wavelength. To detect enough scattering to form spectra, a source of light that will excite more molecules is needed, otherwise the scattering would be too minute to detect and analyze.[36]

When a molecule absorbs energy, as in Stokes scattering, the photon that is emitted will have a lower energy than the original photon. This is the most common form of Raman scattering and therefore the one that the spectrometer is most likely to detect.[37] On the contrary, when a molecule loses energy, as in anti-Stokes scattering, the photon that is emitted will have higher energy than the original photon. See Figure 3 for an illustrative comparison of Raleigh, Stokes, and anti-Stokes scattering. From the shift in frequency that occurs, one can deduce information about the vibrational, rotational, and translational energy of the molecule.

For Raman spectroscopy to occur there must be a change in the polarizability of the molecule upon excitation. The polarizability simply refers the tendency of the electron cloud to become distorted from its usual shape.[38] This distinguishes Raman from IR spectroscopy, which necessitates a change in the dipole moment instead. A dipole moment can be calculated by multiplying the separate charges to the distance between them on the polar molecule or the molecule that has polar characteristics.[38] Because of their differences, Raman and IR can be used in a complementary fashion to learn more about a molecule.
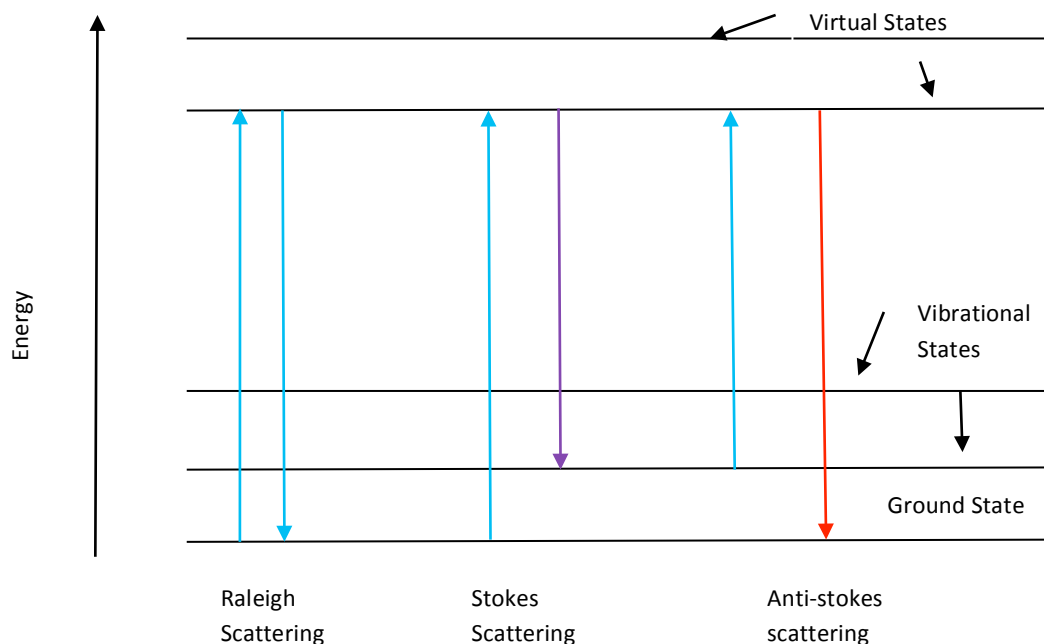
Figure 3: Raleigh, Stokes, and Anti-stokes scattering

Relative energy shifts, denoted as Raman shift with units of wavenumbers, are used in Raman spectroscopy as opposed to absolute wavenumbers. This allows for the same spectrum to be reproduced regardless of the energy of the laser line used. The relative energy change in wavenumbers in the spectra will therefore be the same. Absolute wavenumbers would vary because each laser line has a different wavelength and would thus produce shifts of different wavenumber. For example, a C-H stretching region will appear at about 3000 wavenumbers when using a 514.5 nm laser, as well as when using at 676 nm laser. This is because the shift in energy for a C-H stretching region is constant. Using relative wavenumbers allows one doing the study to compare multiple spectra from an assortment of lasers with ease and also allows the comparison of the Raman vibrational spectra directly to the infrared absorption spectrum of the molecule.

1.5.1 Argon and Krypton Ion Lasers

Argon and krypton ion lasers are commonly used for Raman spectroscopy to excite molecules with photons, from one's choice of various wavelengths available. In the argon ions laser's case, an argon atom collides with two electrons. The first electron will ionize the argon atom and the second electron excites the ionized atom to the 4p level. Afterwards the Argon ion decays to the 4s level. In lasers, stimulated emission is very important. Stimulated emission describes the case in which an excited molecule or atom receives a photon and then proceeds to release two photons, becoming unexcited. The Argon ion laser takes advantage of absorption and stimulated emission to create conditions favorable to light amplification and optical gain.[24] The excitation of different energy levels gives different colors. In this thesis, the argon laser is used for the 514.5 nm laser line (green) while the krypton laser line is used for the 647 nm and 676 nm laser lines (both red).

1.5.2 The Photomultiplier Tube

The photomultiplier is an important component used for Raman spectroscopy because, since there is very little probability that the light will be Raman scattered, any light that is Raman scattered should be multiplied so that the spectrometer can determine its wavelength. This is the purpose of a photomultiplier tube. It works by absorbing electrons on a photocathode surface and then producing free electrons. These electrons be accelerated by a high voltage and will in turn produce secondary electrons until a functional photocurrent is made. Figure 4 depicts the general principle of the

photomultiplier tube. A photomultiplier has more photo efficiency than a CCD (charge coupled device) which is able to read all of the frequencies at once. This makes the CCD camera much faster than the photomultiplier tube. Though the photomultiplier is slower, it is more photo efficient, however. The CCD camera often has more dark noise and electronic noise as well.
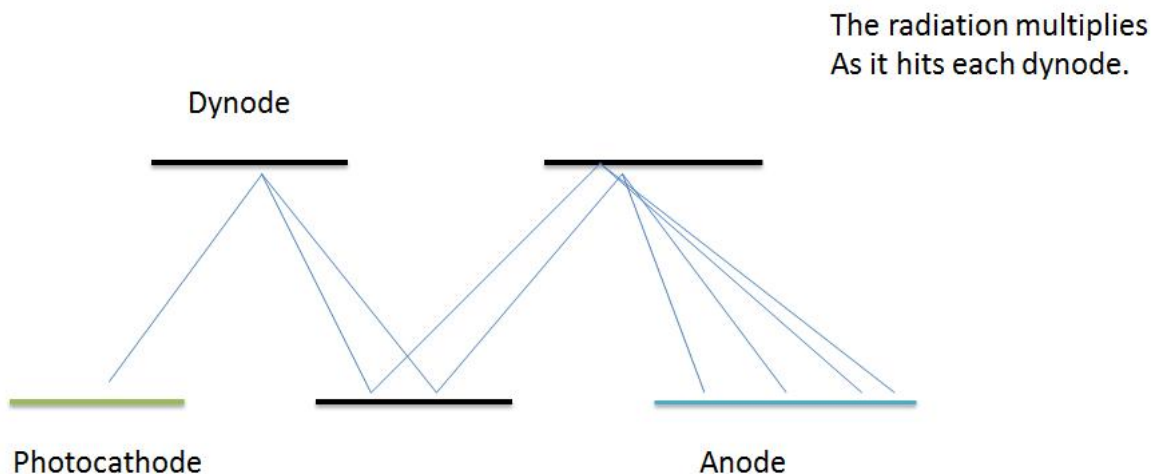

Figure 4: How a photomultiplier tube operates

1.5.3 Diffraction Gratings

A diffraction grating is a prism consisting of parallel, closely spaced grooves. Having many grooves will increase the resolution of the spectra. When scattered light leaves the molecule and enters the Raman spectrometer, the light will hit a grating. This grating diffracts different wavelengths of light at different angles; this allows the Raman spectrometer to record one wavelength at a time. Essentially, the diffraction grating is sorting out the mixture of wavelengths that hit it to allow the spectrometer to interpret it. Different wavelengths come through because of the movement of the grating that disperses light to the

detector. Different intensities are present at different wavelengths because of the spectrum of the molecule under study.[39]

1.6 Surface Enhanced Raman Spectroscopy

Surface enhanced Raman spectroscopy was first used in 1977 when Jeanmaire, Van Duyne, Albrecht, and Creighton found that using a flat metal surface that has been roughened on a nanometer scale greatly enhances Raman spectra. To perform surface enhanced Raman spectrometry, certain metals must be used. Some of these include: gold, silver, copper, or platinum. These metals work because they support optically active surface plasmons, which are oscillations in the conduction electrons. These create an induced electric field that decays exponentially and result in enhancements of the Raman spectra signal of up to 10^{12}.[40] SERS differs from regular Raman spectrometry in that it is highly surface selective and sensitive.[41]

There is a controversy as to what mechanism of SERS enhances the spectra. Two opposing theories explain their proposed mechanisms: electromagnetic theory and chemical theory. The electromagnetic theory is based on plasmons. The plasmons are created when "the incident light excites the electrons gas of the metal."[42] The plasmons, as stated earlier, create a stronger electromagnetic field and thereby induce a stronger Raman signal. The chemical enhancement theory required a transfer of charge from the surface of the metal and the chemiabsorbed species. We plan to study 1H-1,2,3-triazole with SERS in the near future.

2 Vibrational Spectroscopy of 1,2,3-Triazole

2.1 Introduction

Surprisingly, despite the importance of 1,2,3-triazole, few studies employing vibrational spectroscopy to study its intermolecular interactions have been reported. In 1991, Tornkvist calculated the equilibrium geometries and vibrational frequencies of 1,2,3-triazole.[6] In 1998, El-Azhary calculated the optimized geometries, vibrational frequencies, infrared adsorption, and scale factors for 1,2,3-triazole, 1,2,4-triazole, and tetrazole. Raman spectra was obtained for 1,2,4-triazole and tetrazole, but for 1,2,3-triazole their results were compared only to the experimental data in the literature.[43] In 2000, Billes reported a Raman spectra of 1H-1,2,3-triazole using FTIR, FT-Raman, and polarized Raman. Using DFT calculations, he assigned the values of each vibrational frequency to a peak but had great difficulty in accurately assigning them because of the "strong association and tautomerism" of the molecule.[44] Very recently, Bellagamba, et al. explored the structure of liquid 1,2,3-triazole using energy-dispersive X-ray diffraction, molecular dynamics, and FTIR spectroscopy.[31] These authors suggested that both the 1H and 2H tautomers are present in the liquid form. Over the years, much controversy over the tautomerism of 1,2,3-triazole has led to more research in an attempt to discover which tautomer is present in each type of solution. Here, the competition between 1,2,3-triazole bonding with itself versus water is explored and how this compares to tautomerism in the liquid state.

2.2 Methods

2.2.1 Spectroscopic Methods

1H-1,2,3-triazole was obtained from Sigma Aldrich at 97% purity. It was also obtained from TCI at >98% purity. Neither of these was further purified. The Sigma Aldrich sample was used for the initial 514.5 nm, 647 nm, and 676 nm studies of neat 1,2,3-triazole. These laser lines are from a Spectra-Physics Stabilite 2018-RM laser. The triazole sample obtained from TCI was used from then on after the Sigma Aldrich supply was depleted, and was, therefore, used in the mixtures of 1,2,3-triazole and distilled water due to its higher purity. A Labview-controlled Jobin-Yvon Ramanor HG2-S Raman spectrometer was used to survey the sample. The 514.5 nm laser had a power of 600 mW before filter and 400 mW after. The 647 nm laser had a power of 150 mW before and 100 mW after filter. The 678 nm laser had a power of 50 mW before the filter and 25 mW after. An appropriate laser line filter and half-wave plate were used with each laser. The half-wave plate was used to rotate the polarization of the light. The range analyzed ran from 100 to 3500 wavenumbers in the 514.5 nm and 647 nm laser. However, the 676 nm laser analyzed from 100 to 1600 wavenumbers. The scan speed was set to 1 wavenumber per second. To study the effects of hydrogen bonding on 1H-1,2,3-triazole, mixtures of triazole and water were employed. Triazole to water mole fractions of 1.00, 0.85, 0.70, 0.50, 0.30, and 0.00 were analyzed.

2.2.2 Computational Methods

Quantum chemistry calculations were performed on 1,2,3-triazole and molecular clusters involving 1,2,3-triazole and water using the Gaussian 09 software package. The B3LYP/6-311++G(2df,2pd) method and basis set combination were used to optimize geometries and calculate harmonic frequencies. A lack of imaginary frequencies confirmed that all geometries were minima. A custom computer program written using National Instruments LabView was employed to view and analyze the spectra.

2.3 Results

2.3.1 Experimental Results

The use of three different laser lines with samples from two vendors was explored to determine the optimal experimental conditions. Figure 5 compares the spectra of 1H-1,2,3-triazole from Sigma Aldrich obtained using the 514.5 and 647 nm laser lines. It was discovered that the 514 nm laser line caused this sample to fluoresce with time and, therefore, its spectrum has a slight curvature. Over time this sample turned from its original translucent peach shade to a darker peach shade. When higher wavelength laser lines were used, the resulting spectra had much less fluorescence, and the triazole sample did not change colors.

Figure 5: The fluorescence caused by impurities of 1,2,3-triazole can be seen by the curvature of the 514.5 nm laser and the 647 nm laser with fluorescence.

647nm with fluorescence

647nm without fluorescence

514.5nm

Raman Shift (cm^{-1})
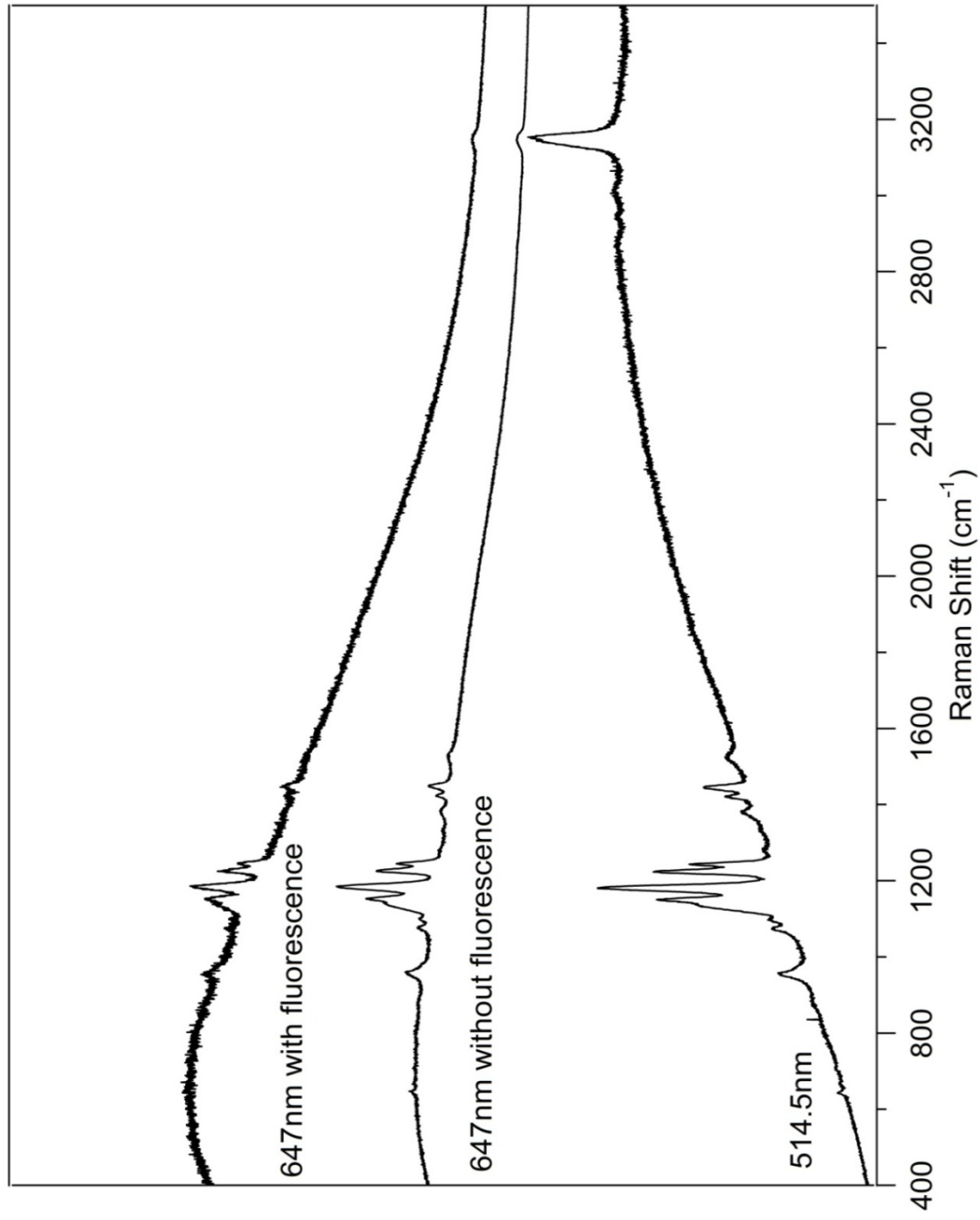
Analysis of a sample that had previously been irradiated with 514.5 nm light using a 647 nm laser line is also shown in Figure 5. Because the sample had already started to fluoresce, the first spectrum obtained by the 647nm laser fluoresced as well. For comparison, a fresh sample of 1,2,3-triazole was also studied, and no fluorescence appeared in the newly obtained spectrum. For the remainder of the experiment, the 514.5 nm laser was used with the purer sample from TCI was used because any slight fluorescence from impurities did not interfere with the results, and using the 514.5 nm laser yielded the greatest signal to noise ratio, as seen in Figure 6. The C-H peak at around 3100 was much more visible when using the 514.5 nm laser, compared to the other lasers in which the peak barely appeared. Further supporting the use of the 514.5 nm laser, Figure 6 depicts three laser lines, 514.5 nm, 647.1 nm, and 676 nm, over a smaller range of the spectrum. The peaks in the 514.5 nm spectrum again have the greatest signal to noise ratio and are the easiest to interpret. The 676 nm laser had the worst signal to noise ratio due to its lower power.

Figure 7 compares Raman spectra of 1H-1,2,3-triazole with aqueous solutions of decreasing mole fraction of 1H-1,2,3-triazole. Several blue-shifting peaks are evident in the spectra. A blue shift is an increase in wavenumber or a decrease in wavelength of a normal mode.[45] Since many of the peaks are overlapped, the spectra were fit to sums of Lorentzian functions in order to determine the locations of the individual peaks. For example, the sum of two Lorentzian functions is:

$$f(X)=Y+Y_0/\pi*(.5*A_0/((X-X_0)^2+(.5*A_0)^2))+Y_1/\pi*(.5*A_1/((X-X_1)^2+(.5*A^1)^2)) \quad (1)$$

Figure 6: Three different laser lines were used in analyzing 1,2,3-triazole. The 514.5 nm had the best signal to noise ratio.
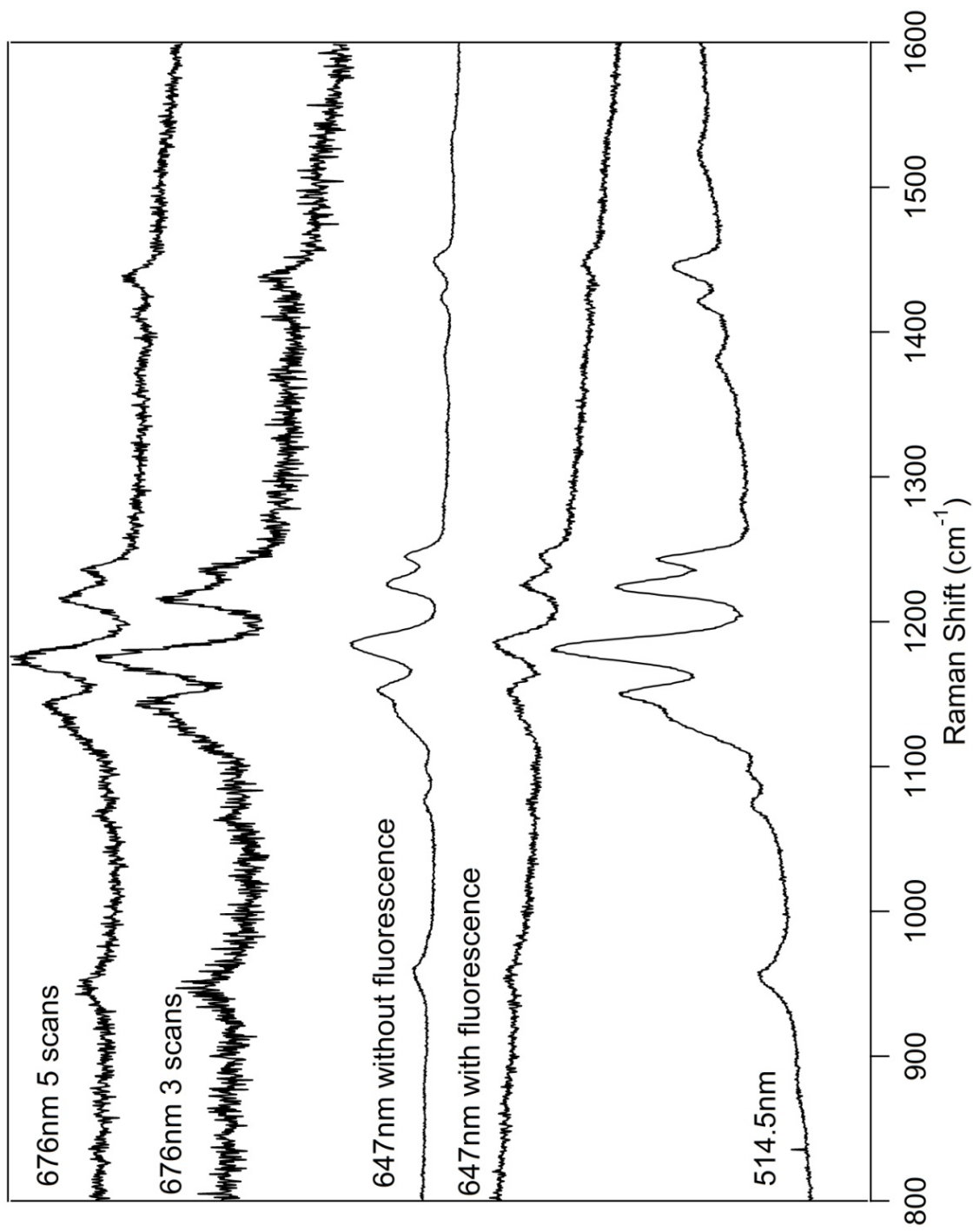
676nm 5 scans

676nm 3 scans

647nm without fluorescence

647nm with fluorescence

514.5nm

Raman Shift (cm^{-1})

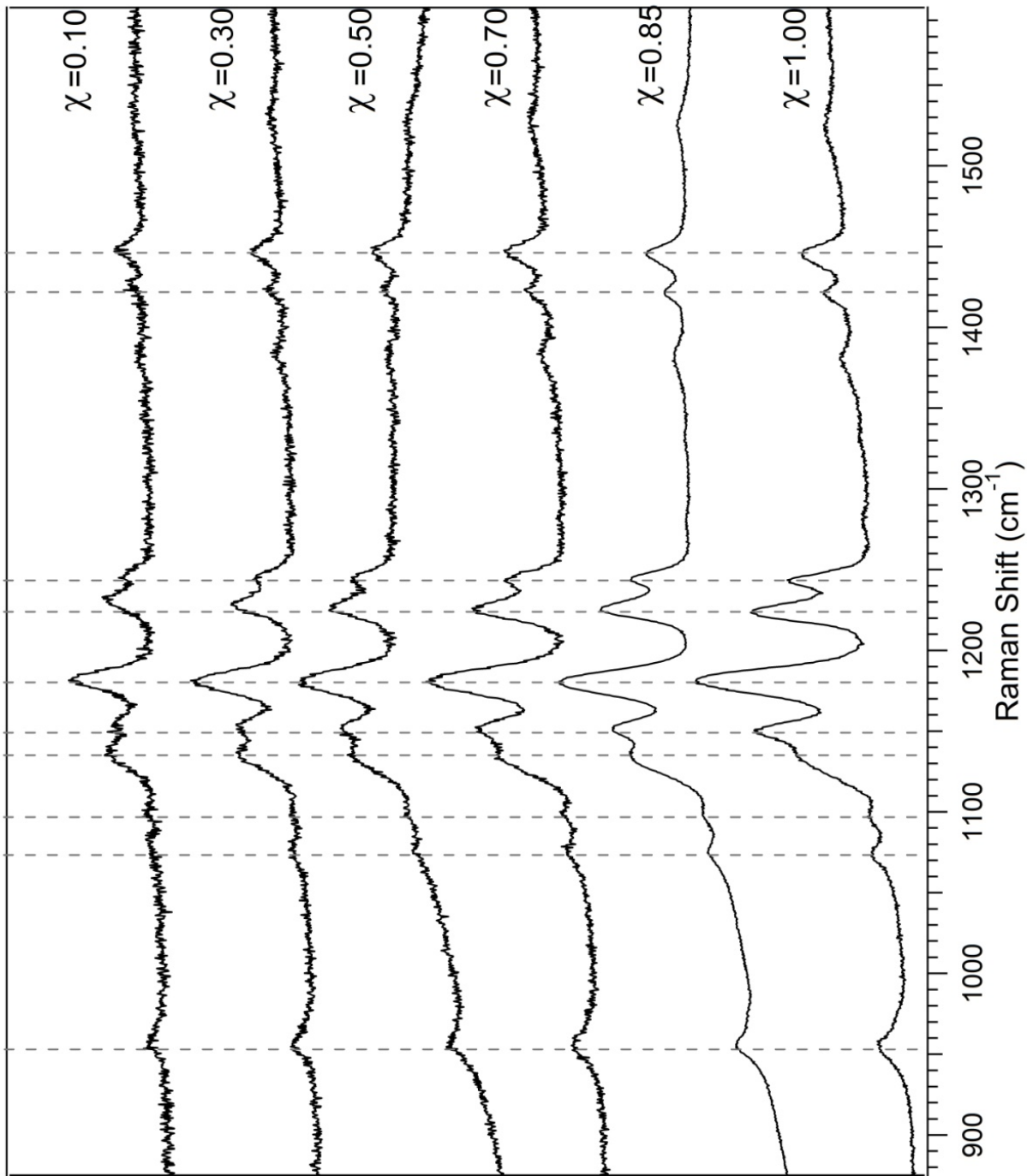800   900   1000   1100   1200   1300   1400   1500   1600

21

Figure 7: Raman spectra of 1H-1,2,3-triazole with aqueous solutions of decreasing mole fraction of 1H-1,2,3-triazole over the range of 850-1600 wavenumbers.

22

where Y represents the baseline photon count. Y_0 is the difference of photons between the baseline photon count and the amount of photons that the top of the peak represents. The same is true of Y_1. A_0 is the width of one peak, while A_1 is the width of another. X_0 and X_1 are the wavenumber locations of each peak in the Lorentzian function. Figures 8-10 show Lorentzian fits for several sections of the spectrum.

Table 1 lists the spectral positions of the various normal modes of 1H-1,2,3-triazole under study in aqueous solutions of decreasing mole fraction as determined from the Lorentzian fits. Analysis of the positions reveals blue shifts of the modes centered at 1132, 1150, 1224, 1243 and 1382, 1422, 1445 and 1525 wavenumbers.

Table 1: Peak centers (in cm^{-1}) as a function of mole fraction of 1H-1,2,3-triazole in aqueous solution.

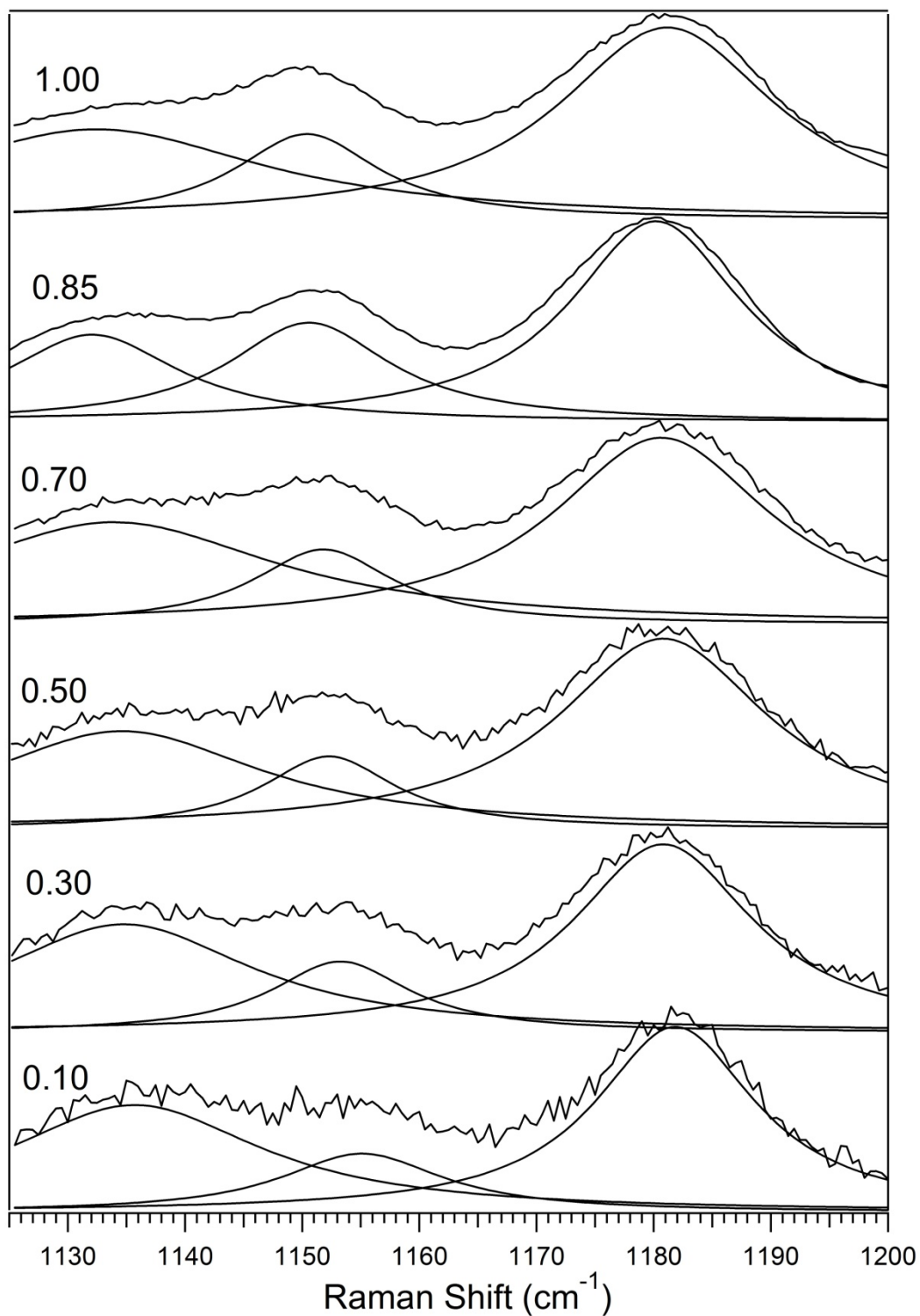| C=C stretch + N-N stretch	1133	1132	1134	1135	1135	1136
N-N stretch + C-H def	1150	1151	1152	1152	1153	1155
C-N stretch	1181	1180	1181	1181	1181	1182
C-N stretch	1224	1226	1225	1226	1228	1231
N=N stretch	1243	1244	1244	1245	1245	1247
C-N stretch + C-H def	1382	1381	1384	1380	1385	1384
C-N stretch + C-H def	1422	1422	1423	1424	1424	1427
C-N stretch	1445	1445	1446	1445	1447	1448

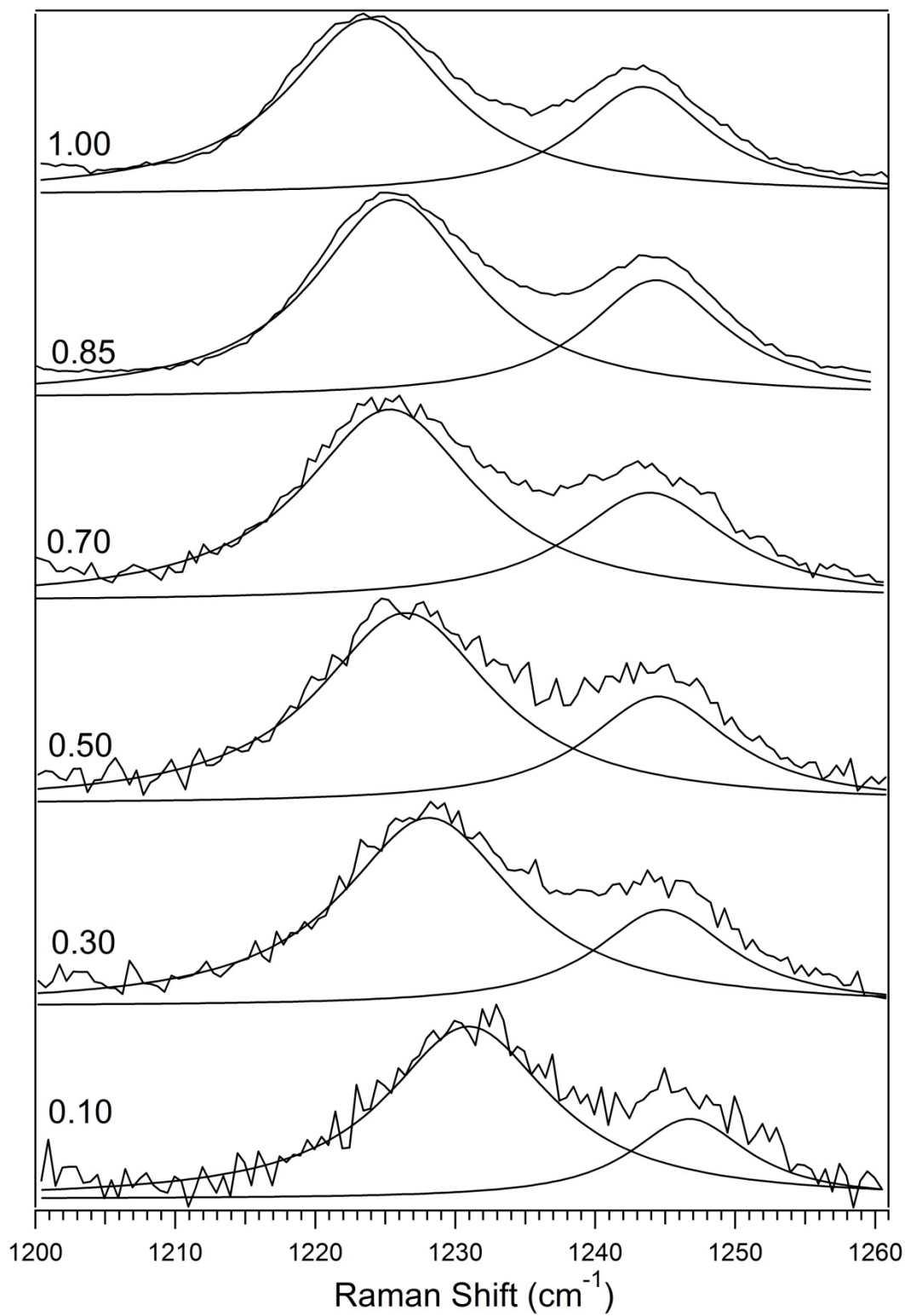**Figure 8:** Lorentzian fits for the 1125-1200 wavenumber range

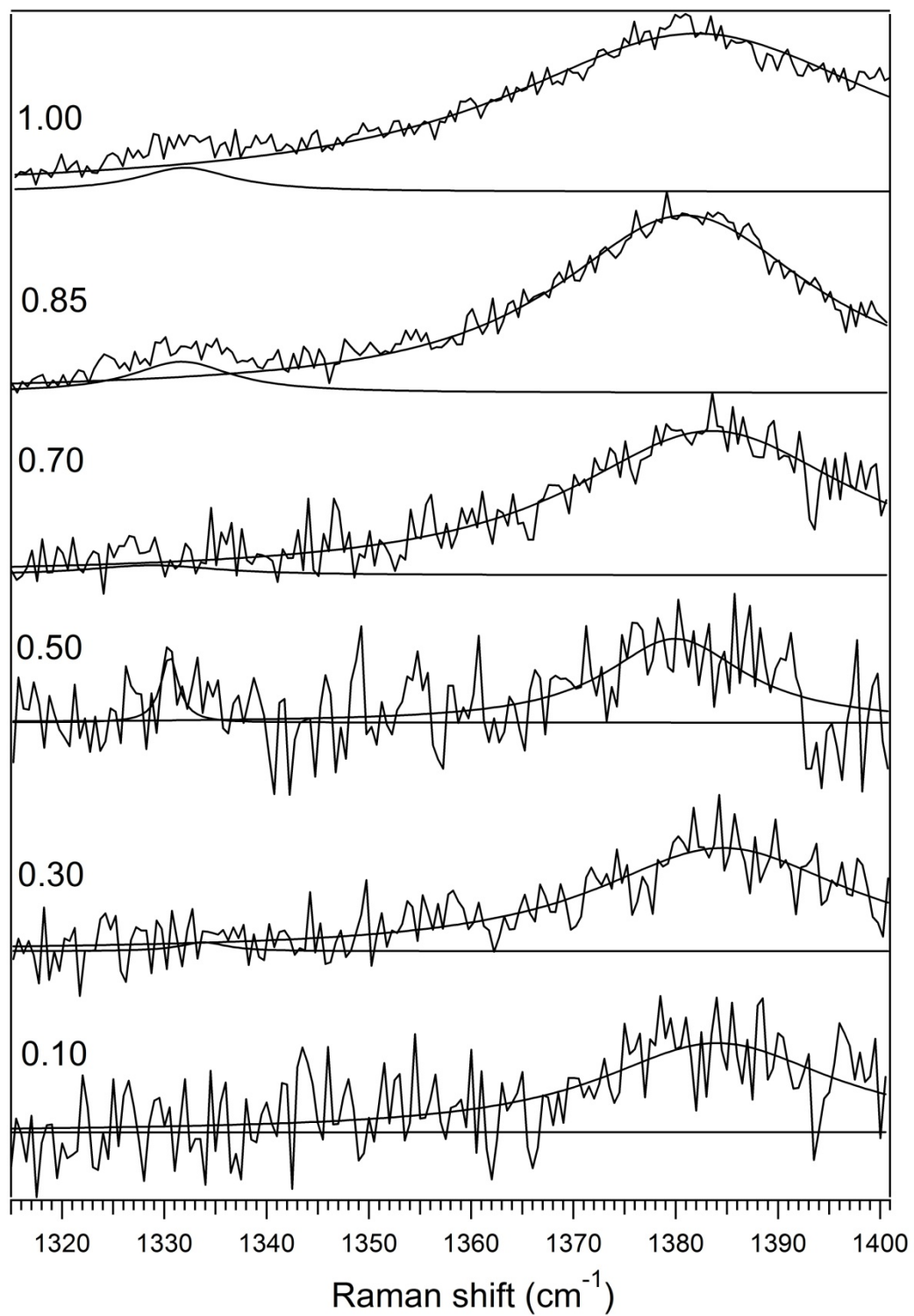**Figure 9:** Lorentzian fits for the 1200-1260 wavenumber range

Figure 10: Lorentzian fits for the 1315-1400 wavenumber range

2.3.2 Theoretical Results

In order to analyze the spectroscopic results, the geometries of molecular clusters involving 1H-1,2,3-triazole and water were optimized and their vibrational frequencies and Raman intensities were calculated. Figure 11 shows the optimized geometries of 1H-1,2,3-triazole and 1H-1,2,3-triazole hydrogen bonded to water molecules. Figure 12 displays 1H-1,2,3-triazole dimers and 1H-1,2,3-triazole dimers hydrogen bonded to water molecules. In order to investigate possible contributions from 2H-1,2,3-triazole to the Raman spectra, its geometry was also optimized and its Raman spectrum simulated. Table 2 contains the energies of each optimized structure.
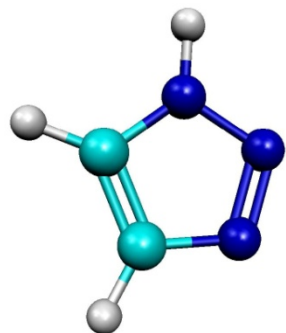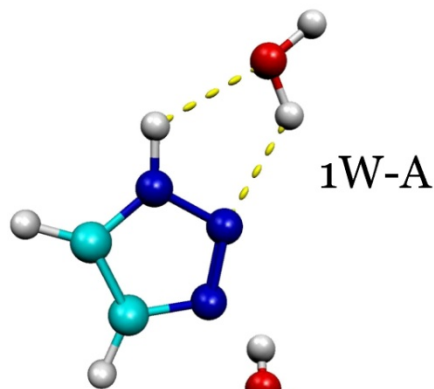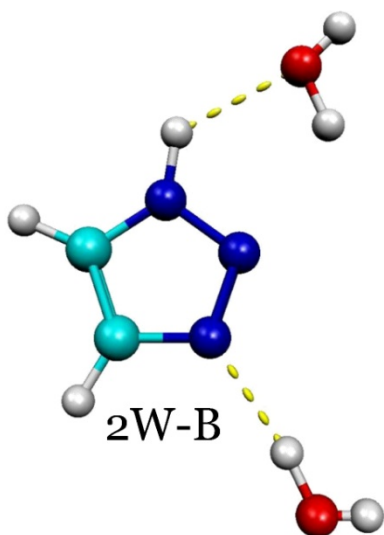
1H- 1,2,3-triazole

2H-1,2,3-triazole

1W-A

1W-B

2W-A

2W-B
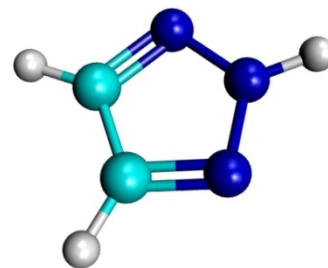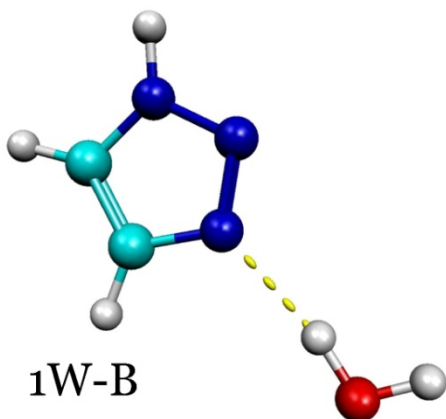
3W

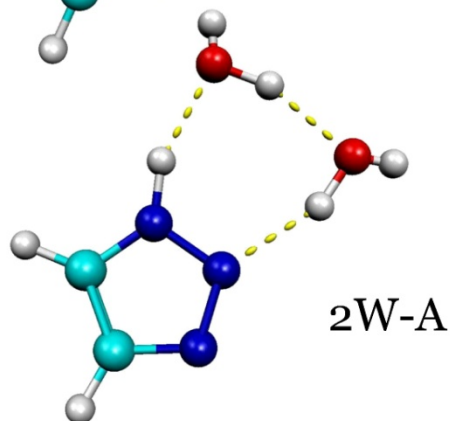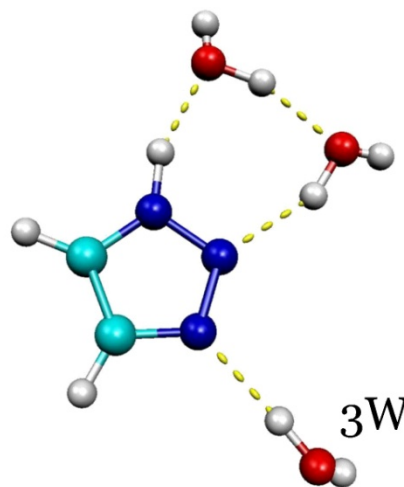**Figure 11:** Optimized structures of 1H-1,2,3-triazole hydrogen bonded to water molecules.

D-A

D-B-1W-A

D-B

D-B-1W-B

D-B-3W
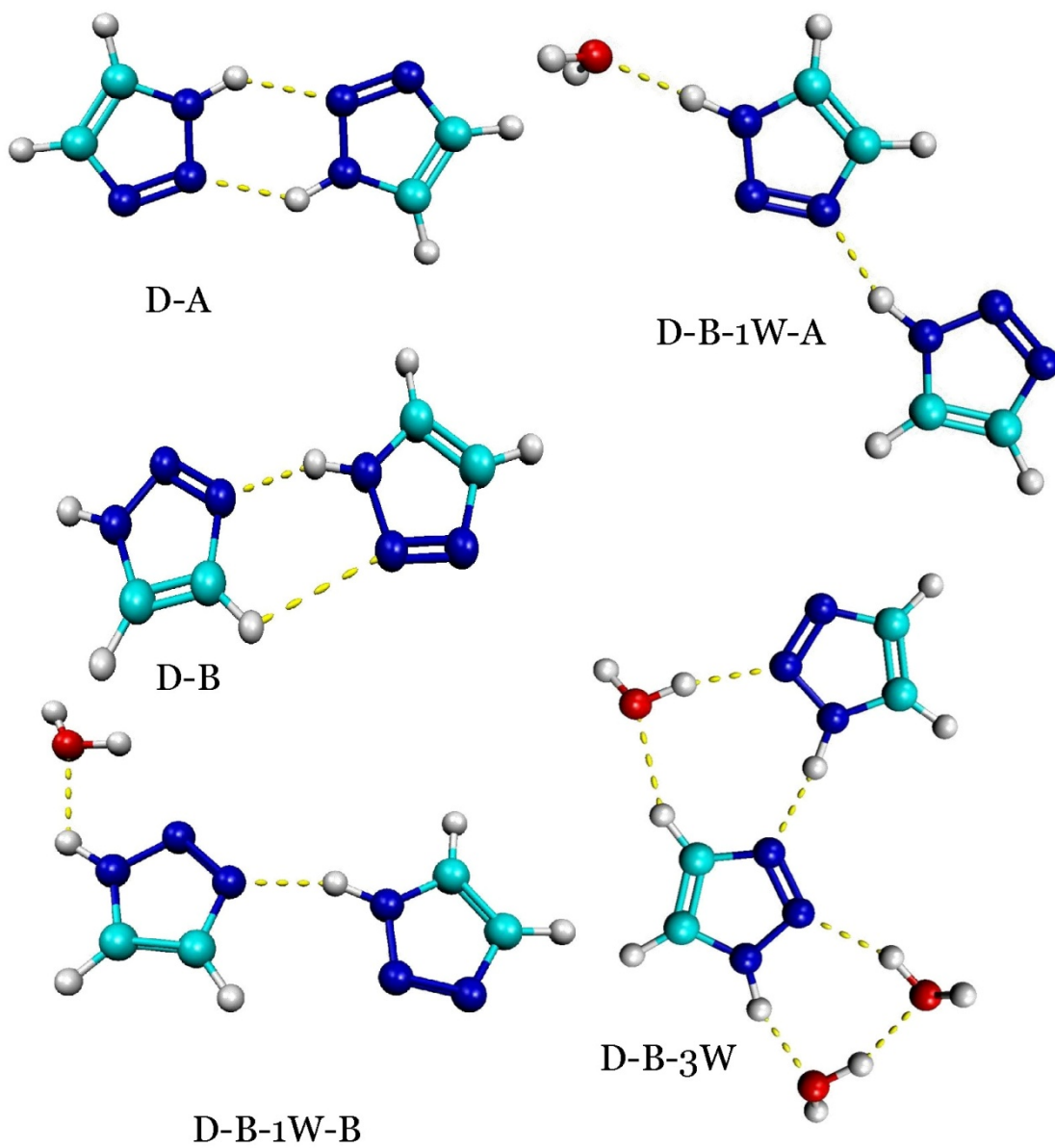
Figure 12: Optimized structures of 1H-1,2,3-triazole dimers and 1H-1,2,3-triazole dimers hydrogen bonded to water.

Structure	Hartrees	kcal/mol
1H-1,2,3-triazole	-242.309100675	+4.25
2H-1,2,3-triazole	-242.315875576	
1W-A	-318.784211226	0.00
1W-B	-318.782214210	+1.25
2W-A	-395.268543097	0.00
2W-B	-395.257412087	+6.98
3W	-471.741493220	
D-A	-484.638416583	0.00
D-B	-484.632674887	+3.60
D-B-1W-A	-561.107843818	0.00
D-B-1W-B	-561.107591144	+0.16
D-B-3W	-714.069614316	

Table 2: Absolute and Relative Energies of Molecular Clusters Studied Here

2.3.3 Comparison of Experiment to Theory and Discussion

Figure 13 compares the Raman vibrational spectrum of 1H-1,2,3-triazole taken using the 514.5 nm laser line to a simulated spectrum of 1H-1,2,3-triazole using the B3LYP method and the 6-311++G(2df,2pd) basis set. These spectra, however, do not agree very well. The experimental spectrum contains several additional peaks that the simulated does not.

Because of the controversy surrounding tautomerism in 1,2,3-triazole, both a 1H-1,2,3-triazole simulated spectrum and 2H-1,2,3-triazole simulated spectrum are compared to the experimental data in Figure 14. Figure 14 suggests that neither tautomer is a good match for the data. In order to eliminate the possibility that a mixture of the two tautomers is indeed the cause of the spectra, the Raman spectrum of a fifty-fifty mixture of 1H and 2H-1,2,3-triazole was simulated and compared to the experimental data and is shown in Figure 15. Although there are additional peaks due to the presence of the two tautomers, the agreement between experiment and theory is still poor.

To explore the possibility that dimers of 1H-1,2,3-triazole are dominating the liquid Raman spectrum, calculations on 1H-1,2,3-triazole dimers were performed. Figure 16 compares the simulated spectra of the N2 dimer and N3 dimer with the experimental spectra of 1H-1,2,3-triazole. Although the N2 dimer is slightly energetically more stable, the simulated spectrum for the N3 dimer better matches the experimental data. Figure 17 compares the experimental

Raman spectrum of liquid 1H-1,2,3-triazole with both the simulated fifty-fifty mixture of the 1H and 2H tautomers and the N3 dimer. Very good agreement between the experimental Raman spectrum of 1H-1,2,3-triazole and the simulated spectrum of the N3 dimer suggests that formation of molecular dimers in the liquid state dominates intermolecular interactions.

Figure 18 compares the experimental Raman spectrum of the 0.10 mol fraction mixture of 1H-1,2,3-triazole and distilled water with the simulated spectrum of the N3 dimer hydrogen bonded to one water molecule. Table 3 compares the maximum observed experimental shifts to the theoretical shift in this structure (D-B-1W-B). The excellent agreement between the experimental and theoretical blue shifts and the experimental Raman spectrum of the 0.10 mol fraction solution of 1H-1,2,3-triazole and distilled water with the simulated spectrum of N3 dimer and water suggests that even upon dilution, molecular dimers still dominate liquid structure.

	Experimental	Theoretical
C=C stretch + N-N stretch	+3	+7
N-N stretch + C-H def	+5	+7
C-N stretch	+1	+2
C-N stretch	+7	+2
N=N stretch	+4	-1
C-N stretch + C-H def	+2	-1
C-N stretch + C-H def	+5	+14
C-N stretch	+3	0

Table 3: Experimental and Theoretical Shifts

Figure 13: Experimental spectrum compared to the simulated spectrum of 1H-1,2,3-triazole.
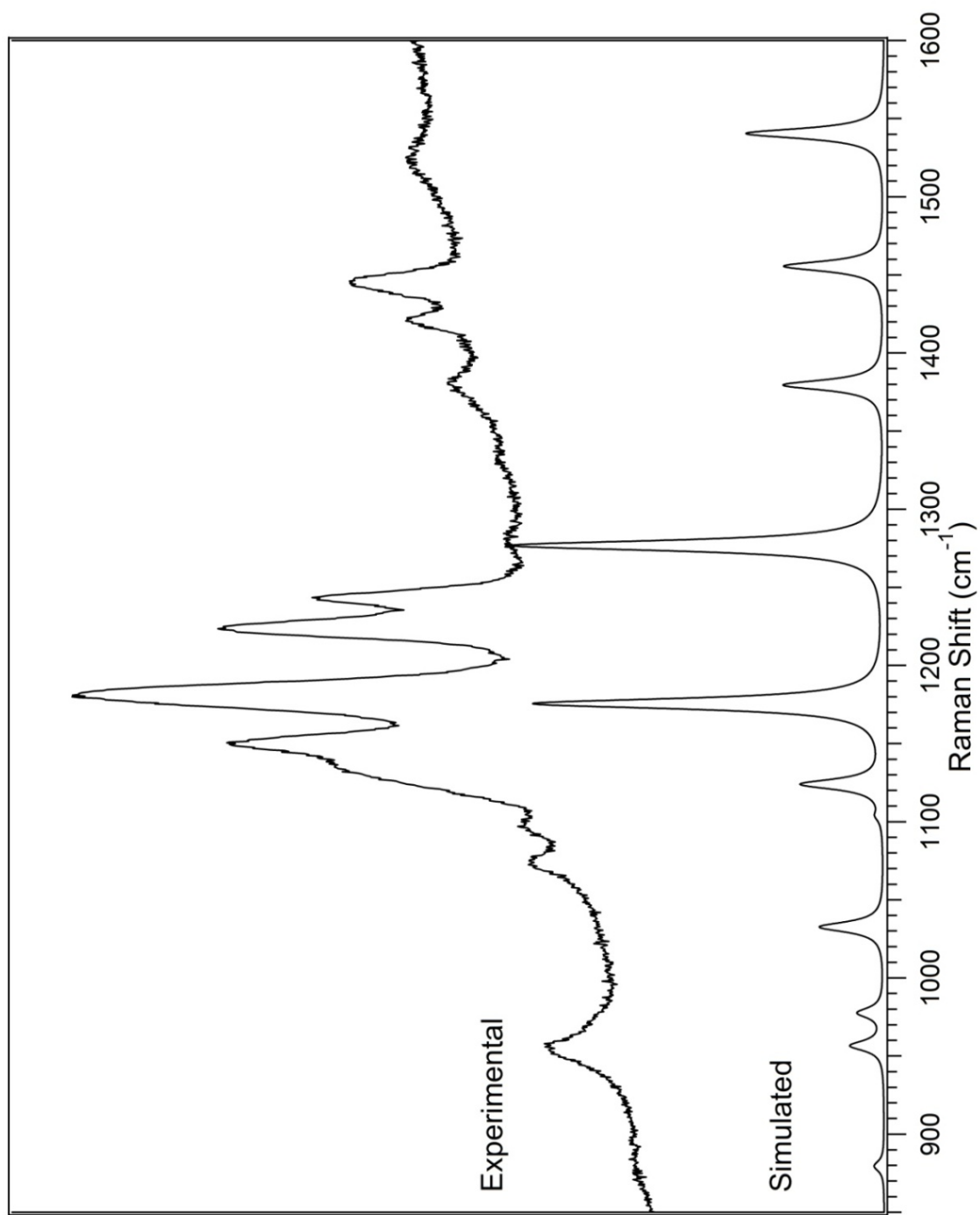
Figure 14:
Simulated 1H and 2H-1,2,3-triazole are both compared to experimental data..
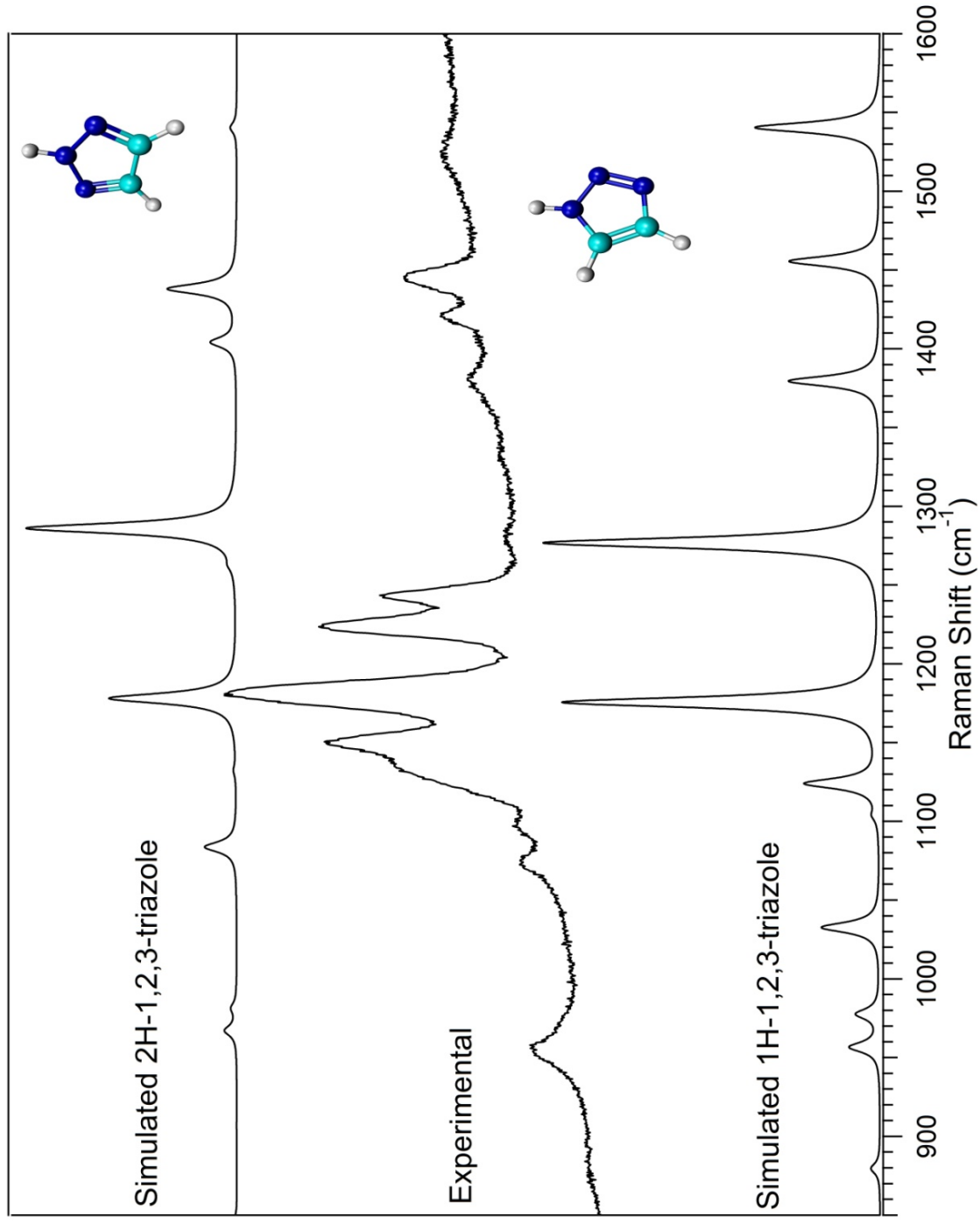
Figure 15:
Simulated 50/50 mixture of 1H and 2H-1,2,3-triazole compared to the experimental data.

Figure 16: The simulated spectra of the N2 and N3 dimers are compared to the experimental data.

Figure 17: A comparison of a simulated spectrum of 2H-1,2,3-triazole and a simulated spectrum of an N3 dimer to the experimental data.

Figure 18: 0.10 mol fraction solution of triazole and water compared to a simulated spectrum of an N3 dimer with water

38

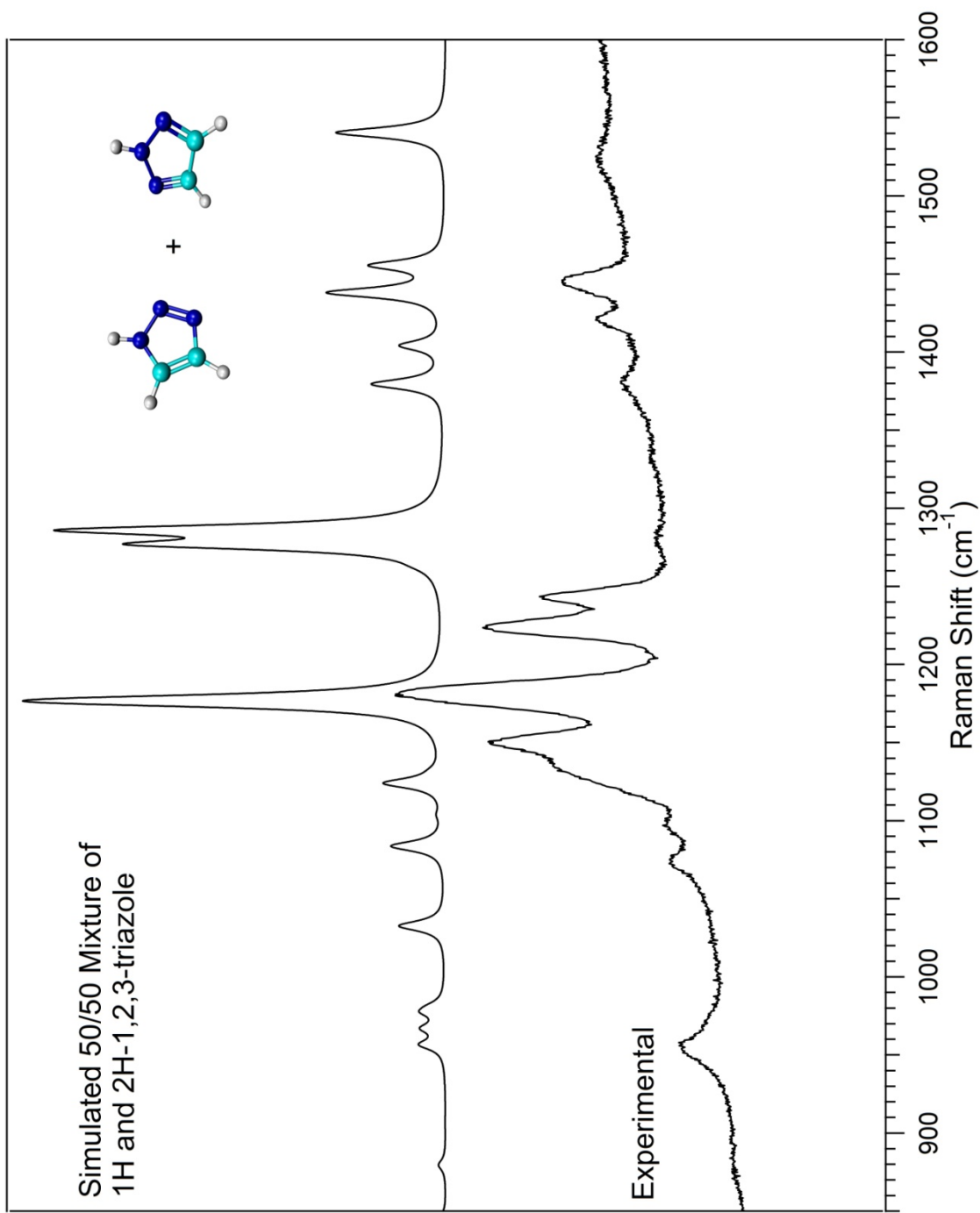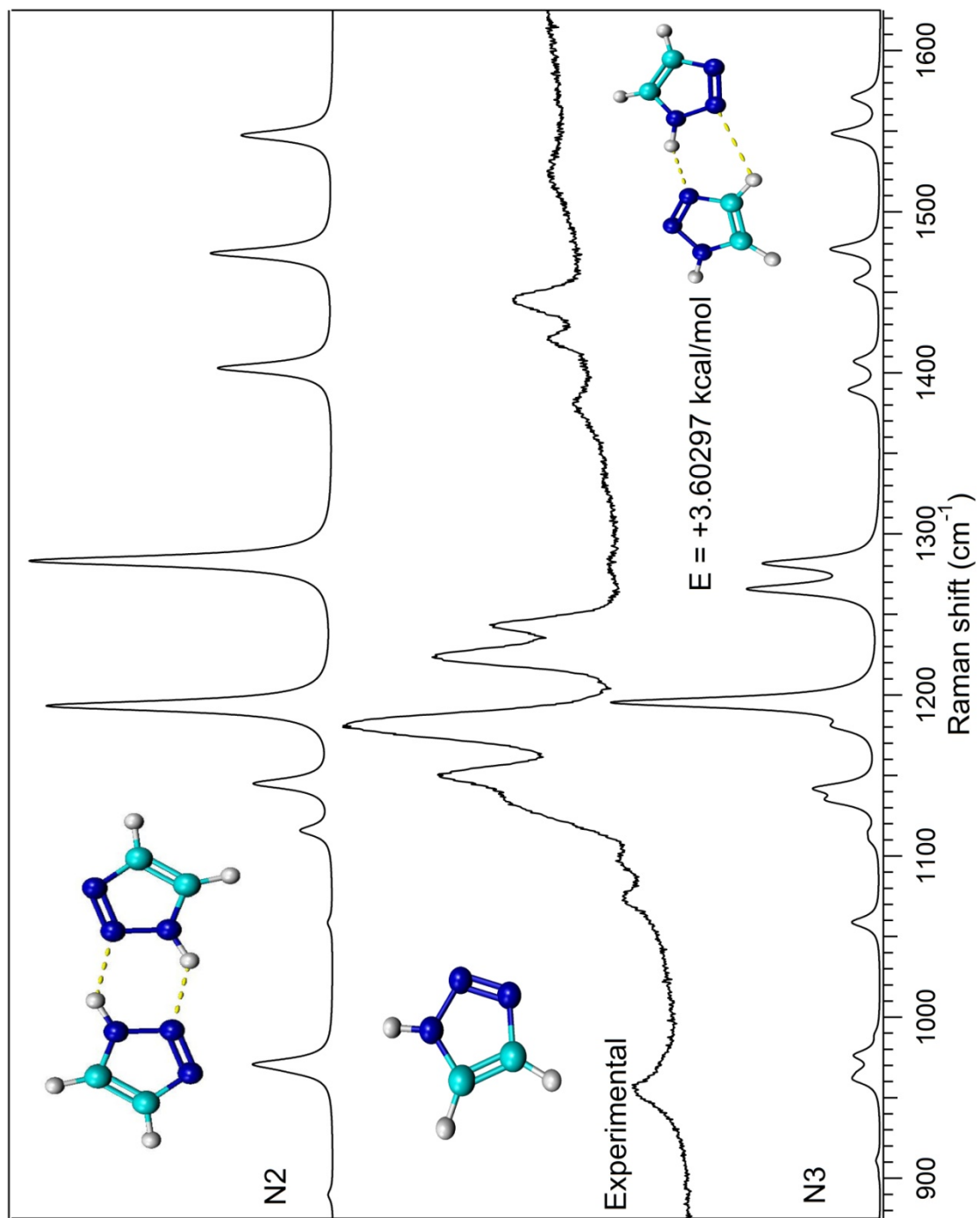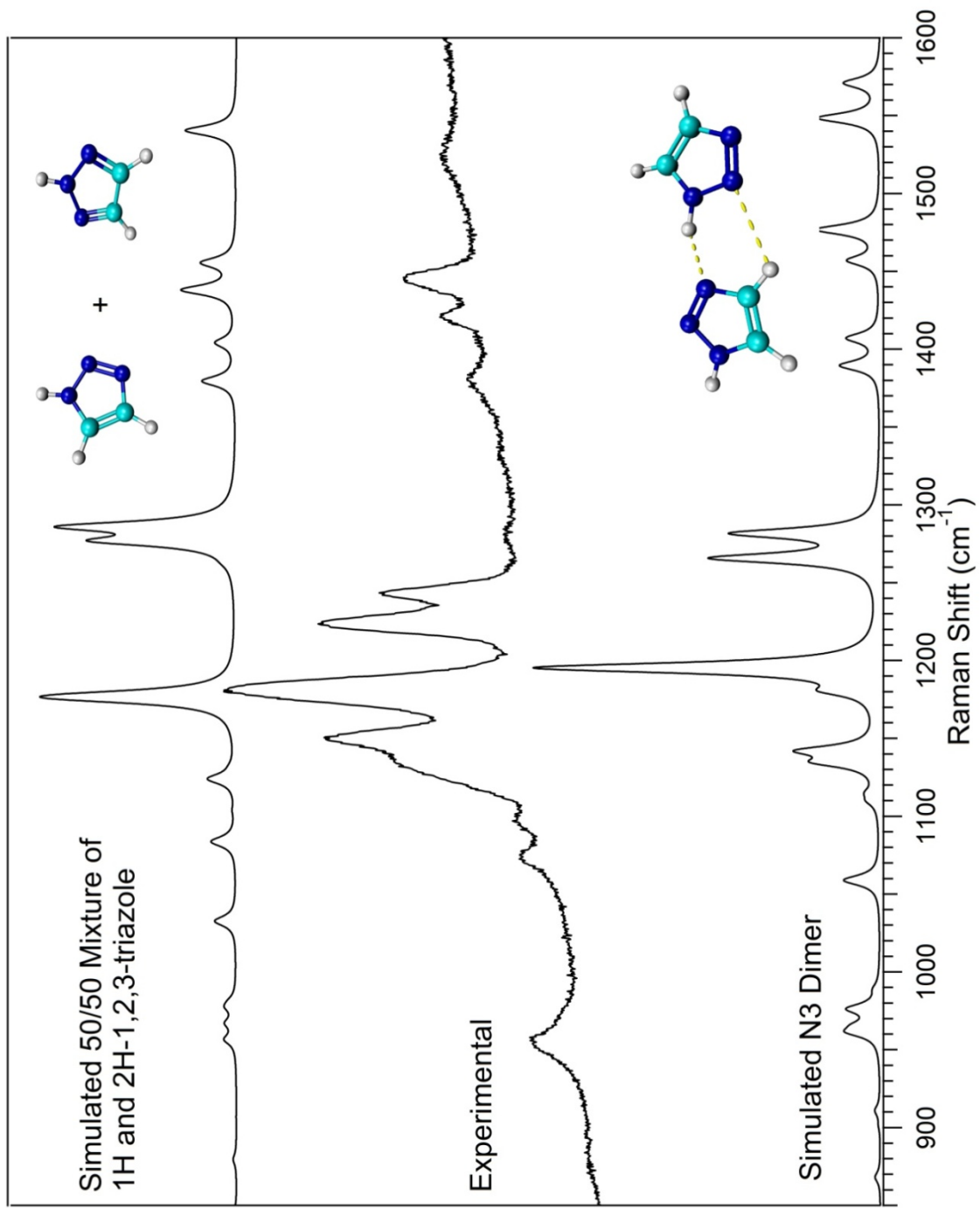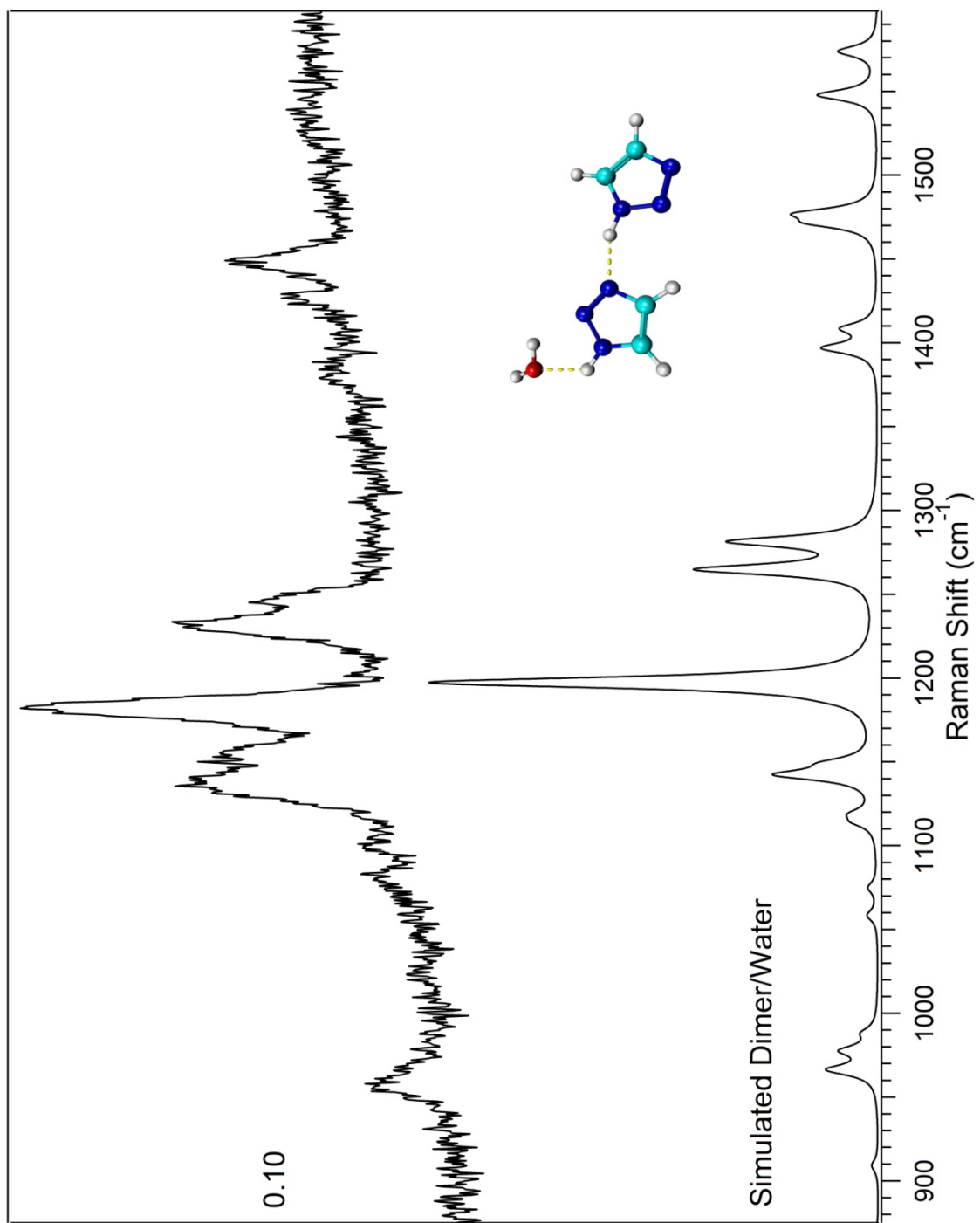Neither the simulated spectrum of 1H-1,2,3-triazole nor 2H-1,2,3-triazole had vibrations at 1224 or 1243. They each had only one vibration in that region. The vibrations at 1224 and 1243 are N=N stretches. Whereas a single molecule of triazole will have only one N=N stretch, a dimer will have two. This explains the discrepancy between the simulated spectra of monomers versus the experimental data collected here.

2.3.4 Conclusions

The hydrogen bonding interactions in 1,2,3-triazole are greatly affected by dimers of the molecule. Dimers must be taken into account because the molecules of 1H-1,2,3-triazole interact with each other strongly, forming hydrogen bonding networks with themselves. If dimers are not considered, the simulated spectrum of aH-1,2,3-triazole does not have a sufficient number of peaks to match the experimental data. The spectra of 1H-1,2,3-triazole dimers, however, is almost an exact match. Therefore, dimers, rather than tautomerism, play the largest role in how 1H-1,2,3-triazole vibrates and interacts with other molecules.

When in water, 1,2,3-triazole forms dimers that interact with the water molecules as well. There is a competition between the water molecules and dimer formations, as the binding sites are limited. The simulated spectrum of a dimer in water matched the spectrum of a 0.10 mol fraction of triazole and water. This leads to the conclusion that dimers are present in aqueous solution and contribute to the Raman spectrum significantly.

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