Chirped Pulse Rotational Spectroscopy of Small Molecule Clusters

Thesis by
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ABSTRACT

Despite the ubiquity of water and alcohol mixtures in every realm of science, the hydrogen bond network governing the unique properties of these mixtures is still under investigation. To aid in the determination of hydrogen bond energetics and dynamics in alcohol and water mixtures, herein a ground up approach studying small alcohol:water clusters is presented. Novel instrumentation for chirped pulse Fourier-transform microwave spectroscopy was developed, and subsequently benchmarked against the detection and characterization of ethanol and water trimers. From there, cluster size was gradually increased, first studying ethanol and water tetramers, then switching to methanol for larger cluster studies of pentamers and hexamers. Throughout this thesis, the over-arching questions as to microaggregation in clusters and trends in geometry and relative energy ordering were investigated, and evidence supporting the facile mixing of small alcohols and water is presented at the few-molecule cluster scale. In the final studies of methanol and water hexamers, the first '3-dimensional' bonding motifs of methanol and water clusters are observed, marking the transition from the planar conformers of small clusters to the complex and higher cooperativity bonding patterns in larger clusters and in bulk mixtures.

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S.E. Dutton gathered and analyzed all data, and prepared publication.

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Chapter 1

INTRODUCTION

1.1 Motivation

Of the fundamental building blocks of chemistry, the hydrogen bond is perhaps the most vital. Chemistry is interaction; hydrogen bonds encapsulate this property, as they live in the liminal space that is weaker than fully covalent interactions and ionic bonds, yet stronger than Van der Waals forces. It is this unique type of bond that allows for DNA to form its iconic helical structure, that keeps water a liquid on the Earth's surface, and that governs protein folding, thus determining biocompatability and biotic architecture (Lenton et al., 2018; Soper et al., 2005; Nyamweya and Abuga, 2021).

Given the importance and vast applicability of hydrogen bonds, their study has been a focus of physical chemists for decades. Hydrogen bonds have been explored in a myriad of substances, in both liquid and gas phases, all in an effort to characterize the potential energy surfaces of these bonding interactions accurately, and thus describe and predict the observed chemical and physical behavior (Abuga and Nyamweya, 2021; Finneran et al., 2015; Pérez et al., 2012). Despite this body of work, there still remain open questions; the changeable and transient nature of hydrogen bonding renders it difficult to observe, as the energy of these bonds, around the TeraHertz (THz) scale, lies within a range not easily generated from laser sources; THz frequencies of light lie between the infrared and microwave regions, as seen in Figure 1.1.

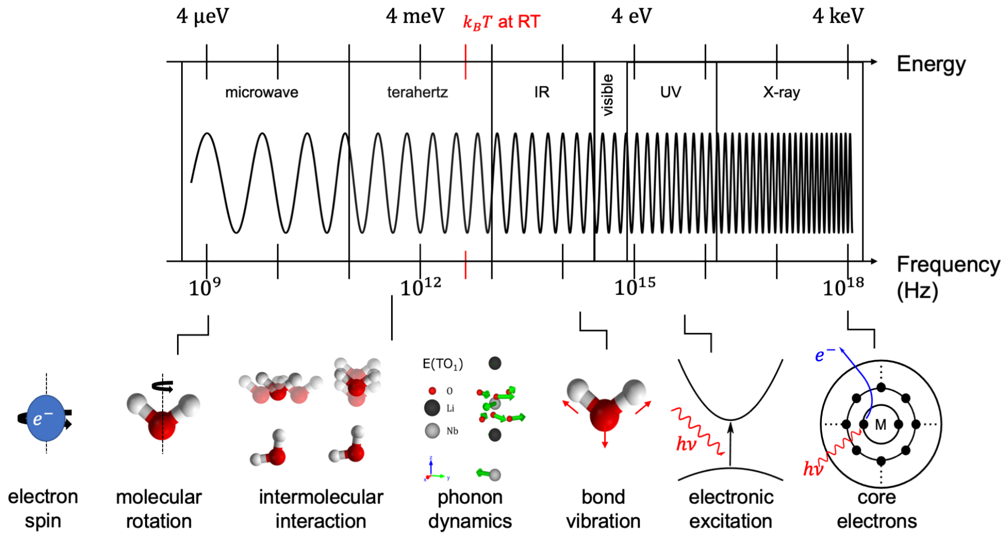


Figure 1.1: Pictorial representation of the regions of the electromagnetic spectrum.

While quantum chemical modeling of hydrogen bonded substances has made strides towards greater accuracy, these models are hindered by the lack of experimental data (Riera et al., 2020; Bosma, Fried, and Mukamel, 1993). This vagary surrounding the behavior and potential energy landscape of hydrogen bonds leads to increased uncertainty in modeling hydrogen bonded liquids for example, which in turn can increase the error in modeling processes that take place in these liquids. One critical example would be modeling and predicting protein folding; this process occurs in an aqueous environment rife with hydrogen bonding opportunities, thus understanding how these bonds play into the macro-scale process is crucial.

One path towards understanding the properties of hydrogen bonds in liquids is to characterize the building blocks of these liquids: small hydrogen bonded clusters.

By quantitatively defining the geometries and relative energies of few-molecule hydrogen bonded sub-units, researchers build towards describing the micro-environments in bulk systems. In fact, recent work in developing force fields for modeling liquid systems follows a similar protocol, tuning the force field to be accurate for small cluster first, then building upon this to model longer range interactions (Riera et al., 2020). Thus, studying these small clusters can inform progress in both experimental and theoretical studies of hydrogen bonded liquids.

To this end, the Blake group has utilized rotational spectroscopy to determine the precise geometry and relative energy ordering of small molecule clusters. Rotational spectra arise from rotational constants, which in turn are determined by the moments of inertia of a molecule or cluster, rendering rotational spectroscopy a well-suited tool for the study of the geometry of small molecule clusters. Thus, by capturing the rotational spectrum of a species, with intensities that depend on the permanent dipole moment, the precise geometry and polarity of the species is characterized. In addition, rotational studies of species with multiple conformers and isomers can allow for determination of the approximate relative energy ordering via observation of relative line intensities, assuming conformers form with similar efficiency. The energy range associated with rotational transitions in small molecules and clusters corresponds with microwave frequencies, lying lower in energy than the intermolecular modes of the THz, as shown in Figure 1.1.

Figure 1.2 depicts an approximate 2D slice of a potential energy surface for a small molecule cluster of interest, in this case, the ethanol tetramer. To determine the

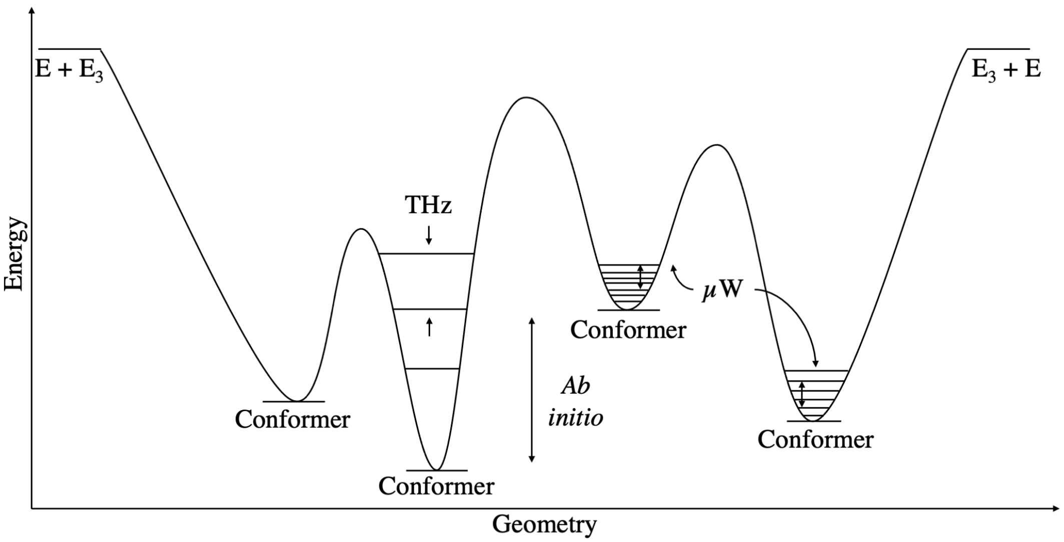


Figure 1.2: Schematic of partial potential energy for ethanol tetramer conformers. Energy levels investigated by microwave (μW) and terahertz (THz) spectroscopies, respectively, are labeled, as are energy differences of stationary points determined *via ab initio* computational methods.

relative energies of minimum energy conformers, or stationary points, as well as the barriers to interconversion between them, computational methods such as density functional theory geometry optimization calculations are performed. In addition to theoretical computations, rotational spectroscopy is required to accurately describe the geometry of these conformers and the energy landscape associated with the rotational transitions of each conformer. Further, THz spectroscopy may then be used to investigate the intermolecular movement associated with interconversion between conformers, ie, the energy barriers between these stationary points. The combination of these methods would then describe the full potential energy surface for a cluster of interest.

Figure 1.2 represents the long term goal of describing small molecule clusters, the potential energy surface of these species, and what can thus be said about the nature of hydrogen bonds in these clusters. Rotational spectroscopy is a crucial part of this long term picture, as it is this technique which yields precise geometric analysis, along with high throughput capabilities enabling the formation and study of multiple conformers simultaneously. In this way, we can consider rotational spectroscopy as our guide along the geometry axis in this potential energy space.

1.2 Chirped Pulse Fourier-Transform Microwave Spectroscopy

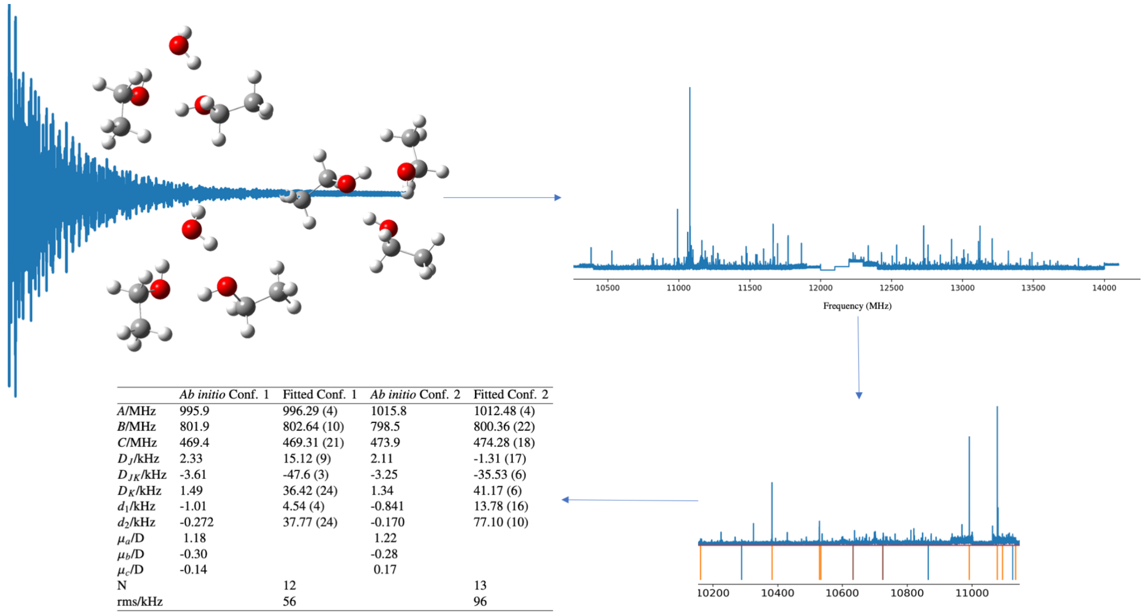
In the last few decades of progress in rotational spectroscopy, one of the most impactful advances has been the implementation of the so-called chirped pulse Fourier-transform microwave approach (CPFTMW), pioneered by the Pate group at the University of Virginia (Brown et al., 2008). Herein, the basics of this technique will be described. Details on our particular implementation are provided in Chapter 2.

As the name implies, the core of CPFTMW is the chirped pulse. As in optical spectroscopy, this term describes the manipulation of a electromagnetic pulse to cover a large frequency range in a pulse duration which is short compared to the dephasing time. In rotational spectroscopy, the chirped pulse is usually digitally generated and then converted and broadcast via a microwave horn to interact with sample. The resulting free induction decay (FID) signal of the sample is collected and digitized for data processing, much as in NMR. The key benefits of using a chirped pulse are the large frequency range that can be covered in a small amount of time, and the low background associated with coherent FID emission. These benefits allow for data collection to be more efficient and allow for higher sensitivity through longer averaging.

This bandwidth is increased even further through the complexation of the signal with a local oscillator (LO) field. This LO mixing not only allows for tunable MW radiation, set by the frequency of the LO, but also doubles the bandwidth of the chirped pulse, as both the sum and difference interactions of the chirped pulse and the LO are generated. In the Blake group, the amplifier range allows for LO frequencies to be chosen to cover anywhere from 2 to 18 GHz. This broadband capability leads to fitting a wide array of rotational lines for each species of interest, improving the robusticity of the resulting fit for the rotational constants.

One challenge associated with this technique is the phase sensitivity of the required coherent averaging of multiple FIDs. If phase drifts between each FID, then the averaged signal will cancel out, resulting in a blank spectrum. To remedy this, careful reference clocking for each component of the circuit used to generate and detect MW radiation is required.

In addition, CPFTMW is supported by calculations, and the interplay between the theoretical and experimental work completed in the Blake lab can lead to both qualitative exploration of the potential energy surface for a cluster in question as well as quantitative characterization of each cluster conformer. The work flow showing the combination of theory and experiment for this type of rotational spectroscopy is shown in Figure 1.3.



	Ab initio Conf. 1	Fitted Conf. 1	*Ab initio* Conf. 2	Fitted Conf. 2
A/MHz	995.9	996.29 (4)	1015.8	1012.48 (4)
B/MHz	801.9	802.64 (10)	798.5	800.36 (22)
C/MHz	469.4	469.31 (21)	473.9	474.28 (18)
D_J/kHz	2.33	15.12 (9)	2.11	-1.31 (17)
D_{JK}/kHz	-3.61	-47.6 (3)	-3.25	-35.53 (6)
D_K/kHz	1.49	36.42 (24)	1.34	41.17 (6)
d_1/kHz	-1.01	4.54 (4)	-0.841	13.78 (16)
d_2/kHz	-0.272	37.77 (24)	-0.170	77.10 (10)
μ_a/D	1.18		1.22	
μ_b/D	-0.30		-0.28	
μ_c/D	-0.14		0.17	
N		12		13
rms/kHz		56		96

Figure 1.3: Diagrammatic workflow for CPFTMW. Time-resolved free induction decay signal is collected, then Fourier transformed to yield rotational spectrum. Observed rotational states are compared to predicted line position for species of interest, and resulting experimental line set is iteratively fit to yield rotational and centrifugal distortion constants.

One particular challenge necessitating both theory and experiment to resolve is the complex rotational spectra of asymmetric tops. In rotational spectroscopy, more symmetric molecules or clusters are better fit with the simple rigid rotor model. Solving the Schrodinger equation for a diatomic or linear rigid rotor yields the energy levels described as such:

$$E_n = J(J+1)Bh$$

$$B = h/8\pi^2 I$$

where B is called the rotational constant, h is Planck's constant, J denotes the quantum number for the rotational angular momentum, and I is the moment of inertia. For example, a diatomic molecule has $I = \mu r_e^2$ where μ is the reduced mass of the system and r_e is the bond length at equilibrium. This calculation of rotational energy states does not include the effects of distortion upon rotation however, so for a diatomic system, the inclusion of a distortion term, D_e changes the rotational energy levels to:

$$E_n = B_e J(J+1) - D_e J^2 (J+1)^2.$$

As the asymmetry of the system increases, the calculation of the rotational spectrum becomes more complex, with more corrective terms to account for distortion and anharmonicity. In addition, asymmetric systems will have three different moments of inertia along each degree of freedom in space, typically tied to the principle axes of the molecule, leading to three rotational constants, referred to as A, B, and C. An example of simple molecules with different degrees of symmetry is shown in Figure 1.4. With asymmetric tops, the rotational spectrum cannot be purely calculated from first principles, but instead must be fit analytically. From experimental data, the three unique rotational constants of a system are fit, as well as distortion constants.

In addition, rotational spectra of clusters can be further complicated by the presence of internal rotors, such as methyl groups. The internal rotation of these methyl groups can couple to the overall rotational tumbling of the cluster as a whole, and thus leads to different rotational energy levels according to the different (usually

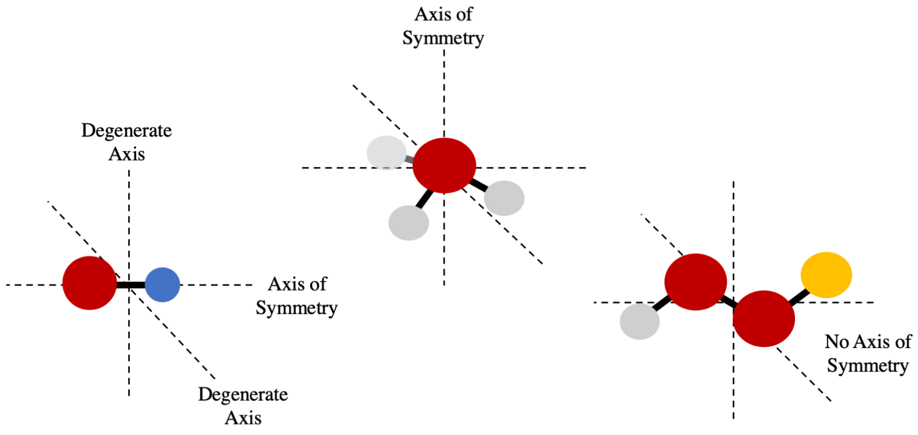


Figure 1.4: Three different types of symmetry in simple molecules. To the left, a diatomic molecule is the simplest rotational species, as it has only one rotational constant determining the spectrum, as does a linear molecule. In the center, a symmetric top, with the 3-fold (or higher) axis of symmetry denoted. On the right, an asymmetric top, with no axis of symmetry is shown (this category also describes molecules with two-fold symmetry axes). Full derivation of the rotational constants requires analytic fitting of the rotational constants to observed rotational modes in empiric data.

nearly degenerate) nuclear spin symmetry states of the internal rotor. This type of splitting will be discussed further in subsequent chapters, as it is of particular relevance to the current area of study.

1.3 Alcohol:Water Clusters

One area for which CPFTMW is ideally suited is the study of molecular structure, or the structure of small clusters. As discussed, the rotational constants of a molecule or cluster are intrinsic to the moments of inertia of that structure; thus, determination of precise rotational constants through rotational spectroscopy leads to determination of the structure. This principle applies even for the complex spectra of asymmetric tops, as the empirically observed rotational states are iteratively fit with the appropriate distortion constants. In addition, experimentation with isotopic substitution can then allow for quantitative calculation of atomic position within the molecule or cluster, to sub-Angstrom precision.

Thus, CPFTMW is a powerful tool for structure determination for all types of symmetric or asymmetric molecules or clusters, provided they are polar, and can help in answering a number of fundamental structure questions. Herein lies the vast applicability of CPFTMW to the study of hydrogen bonding: the precise length, position, and relative energy ordering of the hydrogen bonds holding together small molecule clusters may be determined *via* CPFTMW.

One type of hydrogen bond of particular importance in fundamental chemistry, biochemistry, and industrial processes is hydrogen bonding between alcohols and water. The structure of alcohol and water mixtures at the nanoscale has been difficult to characterize, given that, as previously mentioned, the energy levels of these intermolecular bonds fall in the THz regime of the electromagnetic spectrum. Recent advances in THz generation, propagation and manipulation have made great strides towards describing the molecular environment in alcohol:water mixtures but specific structural questions still remain.

The lack of detailed structural and energetic data for these clusters further impacts the study of these mixtures by limiting the accuracy of molecular dynamics (MD) simulations. Force field development for MD often relies on accurate energy ordering of small molecule clusters in order to build up the potential energy surface of bulk systems. These computational methods can then be used to model such critical processes as solvation or protein folding. With more accurate modeling, computation could then better assist in answering widely applicable biochemical questions such as drug efficacy.

In order to build towards accurate descriptions of small molecule clusters of alcohol and water, the Blake group has utilized a newly designed and novel high-throughput CPFTMW spectrometer to study ethanol:water and methanol:water clusters. This research began with structural studies of mixed ethanol:water dimers with the previous iteration of this instrument. My work has focused on building this newly designed CPFTMW to continue this work, and expanding the use of the instrument to studies of higher order trimers, tetramer, pentamers, and hexamers.

Ethanol was chosen to begin this work for a few reasons. Firstly, ethanol and water mixtures have widespread uses in biochemistry, synthetic chemistry, and industrial processes, making the accurate modeling of small scale interactions highly useful. Secondly, the presence of two carbon centers allows for conformational variation between the trans and gauche geometries in each ethanol monomer, adding complexity to the potential energy surface of available small molecule cluster conformers. In addition, this variation in gauche and trans geometry changes the polarity of the structures, yielding permanent dipole moments in clusters that with all trans ethanol subunits would be nonpolar, and thus invisible to CPFTMW. // In the study of larger clusters, methanol was used as a model small alcohol instead of ethanol to eliminate the added complexity of gauche/trans variation and focus instead on the conformational variation in cluster formation. This change allowed for more direct comparison to the pure water analog clusters, which in turn allowed for determination of net cooperativity changes upon inclusion of methanol into the hydrogen bonding structure of higher order water clusters.

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Chapter 2

INSTRUMENT DEVELOPMENT AND STUDY OF ETHANOL AND WATER TRIMERS

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S. E. Dutton and G. A. Blake (2022). "High throughput chirped pulse Fourier-transform microwave spectroscopy of ethanol and water clusters". In: *Physical Chemistry Chemical Physics* 24.22, pp. 13831–13838. DOI: `10.1039/d2cp01055k`. URL: `https://doi.org/10.1039/d2cp01055k`

2.1 Introduction

Small molecule clusters, though simple in their nature as modest-atom systems, are host to a number of open questions in physical chemistry. One need only examine the long-standing debate surrounding the nature of the hydrogen bond–a topic introduced in introductory chemistry courses–to see the mysteries still encapsulated in the dynamics of few molecule systems.

The hydrogen bond is of vast importance to physical, chemical and biological processes on earth, bottle-necking reaction rates in the atmosphere and determining solvation interactions in condensed phases (Desiraju, 1999; Seinfeld and Pandis, 2016). The importance of this motif is in part due to the weak nature of the hydrogen bond (4 to 40 kcal/mol), allowing bonds to break and form easily (Desiraju, 1999).

A specific area of interest addresses the behavior of hydrogen bonding interactions in alcohol-water mixtures. Condensed phase mixtures of alcohols such as ethanol and water display intriguing behavior, including their negative entropy of mixing. This is indicative of incomplete mixing on a microscopic scale (Juurinen et al., 2011; Soper et al., 2005; Lenton et al., 2018). This behavior has not yet been fully characterized or understood, and the impacts of these properties are far reaching; for example, recent publications investigate the relevance of these physicochemical anomalies to hand-sanitizer effectiveness against COVID-19 (Nyamweya and Abuga, 2021; Abuga and Nyamweya, 2021).

To empirically elucidate the clustering behavior that gives rise to this microaggregation of water and alcohol, the structure determination of small clusters of alcohol and water is a useful proxy system to elucidate the dynamics of bulk mixtures. In the present work, small clusters of ethanol and water are studied, so that accurate structural information may be used to build up to fully molecular bulk models of ethanol and water mixing.

One consideration specific to ethanol clusters, that adds further complexity to accurate modeling, is trans versus gauche conformational variation. Previous studies have demonstrated that weak hydrogen bonding in ethanol and water clusters may additionally stabilize the gauche conformation over the trans (Finneran, Carroll, et al., 2015), which is favored for the monomer. Computational studies of the ethanol trimer have shown a similar trend, with a number of low energy structures with both the trans and gauche conformation of one or more monomers (Malloum, Fifen, and

Conradie, 2020; Masella and Flament, 1998).

To characterize the potential energy surfaces pertaining to such clusters, chirped pulse Fourier-transform microwave (CPFTMW) spectroscopy has become the main tool for the high resolution rotational spectroscopy of gaseous species. Invented by the Pate group at the University of Virginia (Brown et al., 2008), many previous studies have demonstrated the efficacy of this technique for high-sensitivity measurements of pure rotational spectra from cm to (sub)mm wavelengths (Finneran, Holland, et al., 2013; Finneran, Carroll, et al., 2015; Mead et al., 2017; Dian et al., 2008; Evangelisti, Sedo, and Wijngaarden, 2011).

One challenge in past studies with this approach is that sensitivity can be limited by both the pumping speed and by the capabilities of chirp and signal acquisition digital electronics, requiring that gas be pulsed into the chamber to avoid collisional broadening or destruction of clusters from high pressures in the vacuum chamber (Puzzarini, Stanton, and Gauss, 2010; Finneran, Carroll, et al., 2015; Calabrese et al., 2021; Neeman and Huet, 2021). Pulsed gas expansions are effective, but most have a duty cycle of only a few percent.

In this work, a continuous, large aperture expansion instrument for CPFTMW is presented, and compared to pulsed instruments. The efficacy of this technique is further demonstrated through the study of the ethanol trimer and mixed water:ethanol trimers. Rotational spectra and anharmonic *ab initio* calculations are used to guide the rotational constant assignments of the lowest energy conformers of the these clusters. We first turn to a description of the new instrument and results, before describing the nature of hydrogen bonding in the trimers.

2.2 Experimental Methods

The high vacuum chamber design is specifically designed to permit a collinear orientation of the microwave horn and supersonic beam expansion. This orientation allows the same microwave horn to be used for both the broadcast and detection of MW radiation, and optimizes the interaction volume. This instrument is thus an alternative to the 'original' single-nozzle system, as opposed to a multi-nozzle system as implemented elsewhere (Neill et al., 2011).

The high pumping speeds necessary for the desired experiments were achieved via a magnetically levitated Osaka TGKine 3304 Turbomolecular pump in series with an Edwards EM 275 Rotary Vacuum pump, which comes with an additional roughing pump. With this system, the base pressure in the chamber is roughly 10^{-9} torr, and the pumping speed for molecular nitrogen is ~3400 L/s. For Ar or N_2 expansions, the maximum compression ratio is nearly 10^8 (for molecular hydrogen or He the compression ratio drops to 10^{3-4}). With this high pumping speed, gas may be continually introduced into the chamber at 2 atm nozzle pressure without the background pressure rising above $4 * 10^{-4}$ torr, and the high compression ratios achievable mean quite modest backing pumps and roughing lines are required. The resulting mach disk distance, for a pinhole expansion, is at least 1 meter away from the nozzle, ensuring free expansion of the clusters without collisions, and imparting a new ability to probe cluster formation in continuous expansion conditions. A photo of this pump and the new vacuum chamber built for CPTFTMW are shown in Figures 2.1 and 2.2.

As described previously, we employ direct digital synthesis (DDS) (specifically the Analog Devices AD9914 board) to generate a 2 GHz chirp over 1.2 microseconds (Finneran, Holland, et al., 2013). The pulse is low-pass filtered (Mini-Circuits VLP-24) and heterodyned with the local oscillator (LO) frequency from the output of Hewlett-Packard function generator (HP 83260B Series Swept Signal Generator) with a microwave circuit mixer (Marki MIR0726). The resulting pulse contains the sum and the difference of the LO frequency and the digitally generated broadband chirp.

The heterodyned pulse is amplified with a 40 watt solid state amplifier, or SSA (Microsemi RF Integrated Solutions Model LO618-46-T680), and passed through a circulator (Teledyne C-12S63T) to the microwave horn. A diagrammatic representation of the microwave circuit is depicted in Figure 2.3. Note that this diagram does not accurately depict the geometry of the nozzle and gas expansion in the chamber.

The entire circuit is triggered by a digital delay generator (Stanford Research Systems Model DG535 4 Channel Digital Delay Generator). For signal detection, a waveform is sent to an arbitrary waveform generator (Stanford Research Systems Model DS 340 15 MHz Frequency Generator) to trigger the AD9914 DDS board every 20 microseconds, so that an 18 microsecond FID is collected for each microwave pulse.

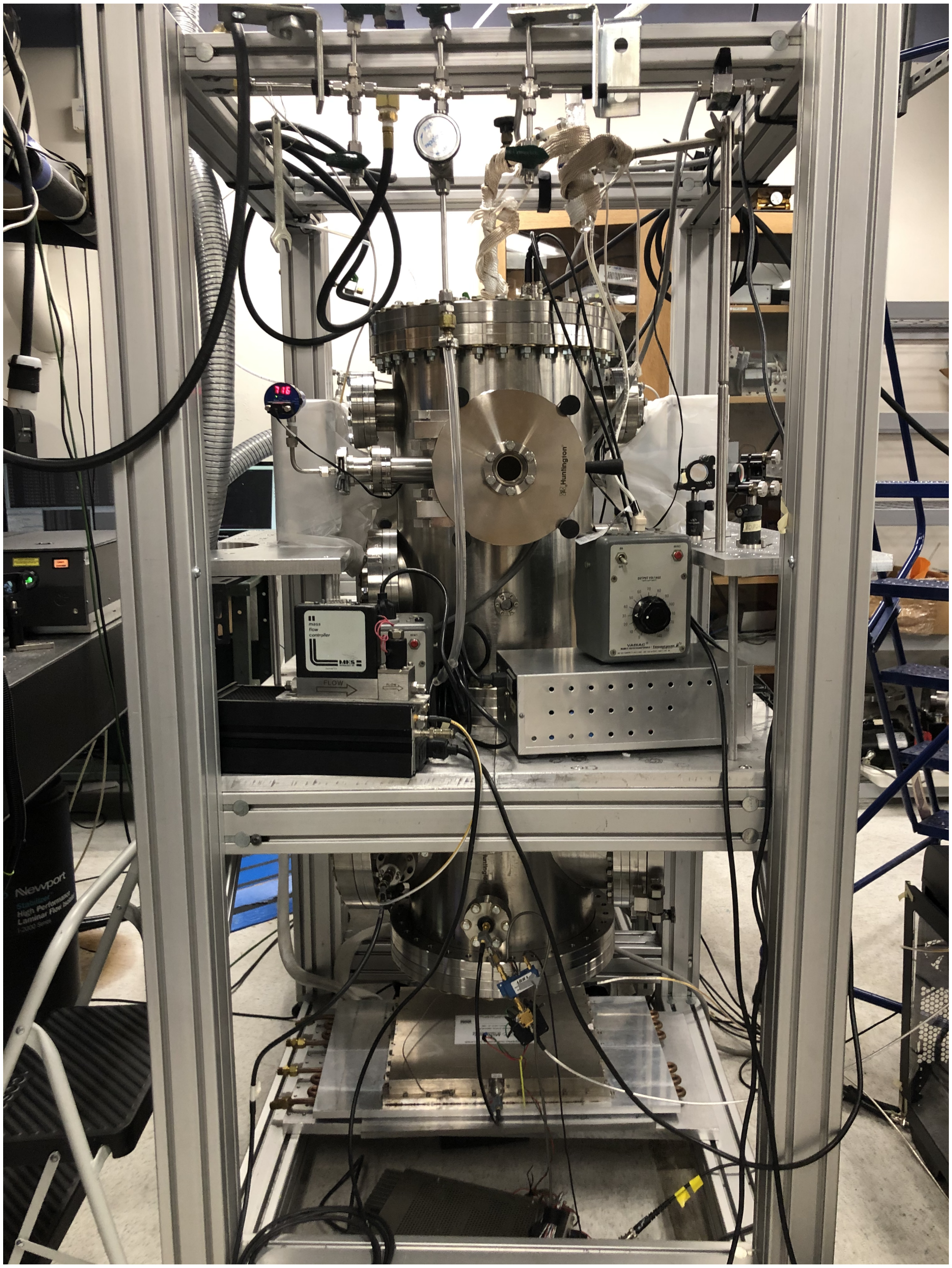

Figure 2.1: Front view of the vacuum chamber built for CPFTMW. THz frequency comb to be integrated in future separate work runs right to left across the image. Gas samples are introduced through the top of the chamber, while microwave horn sits in the bottom.

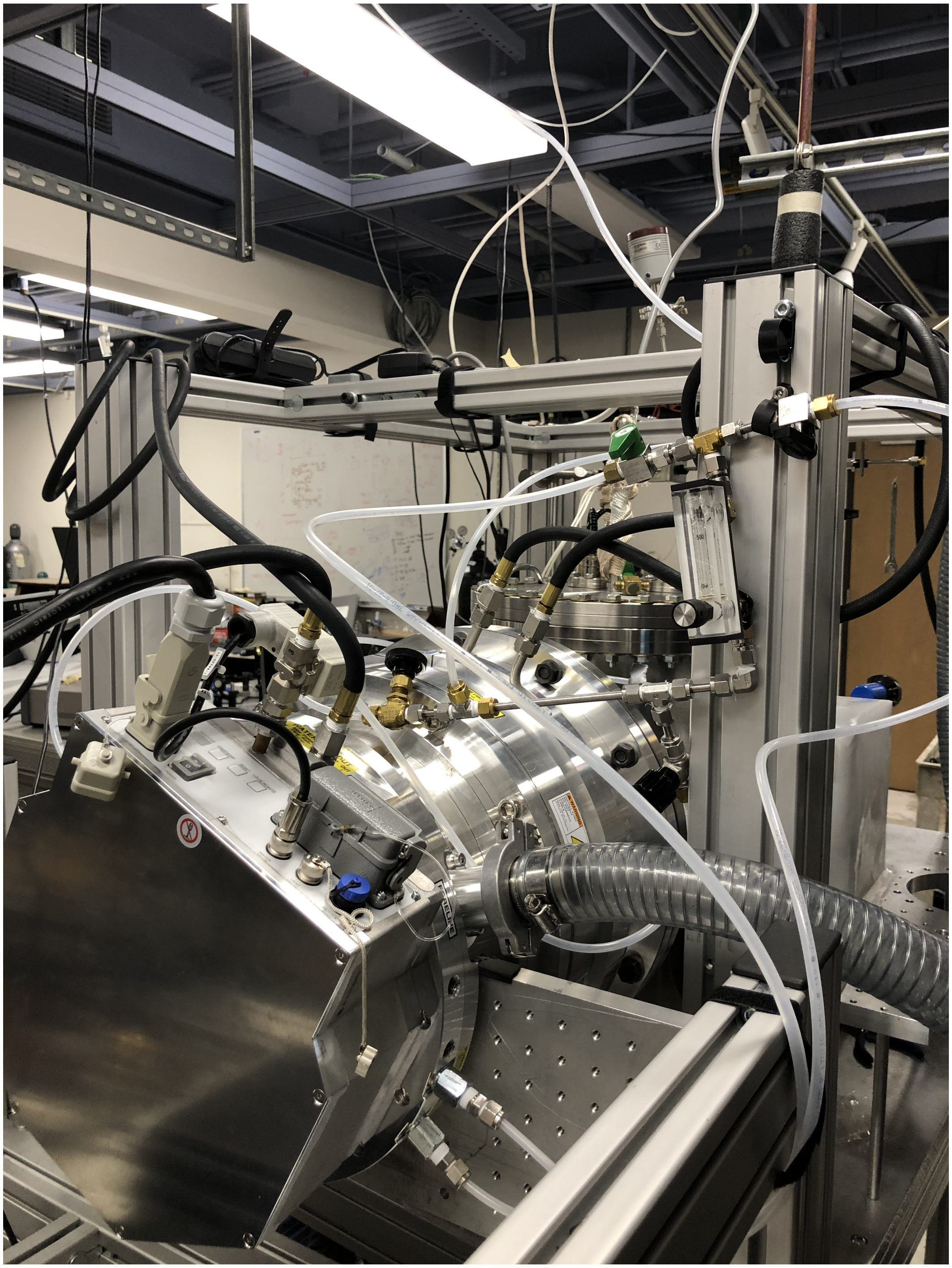

Figure 2.2: Photo of the turbomolecular pump mounted on the ‘back’ of the vacuum chamber, perpendicular to the axis of the sample beam expansion and the microwave horn.

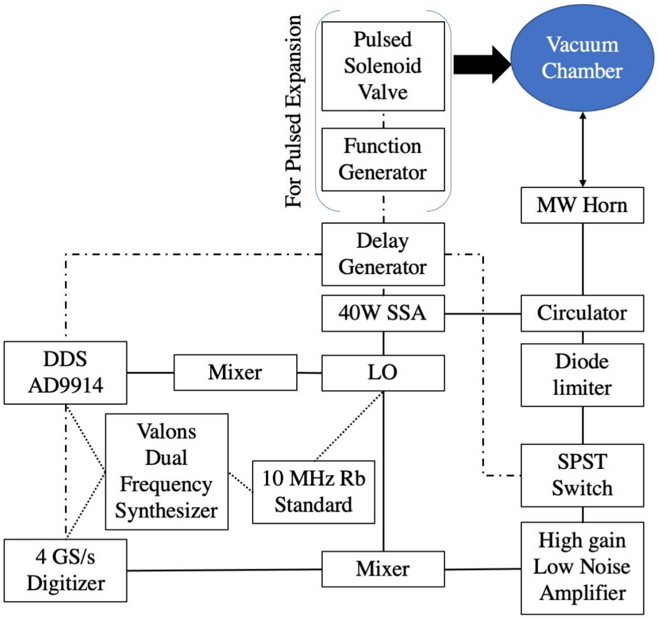

Figure 2.3: Schematic of the microwave circuit built. Solid lines represent SMA cables transmitting the microwave signal. Dotted lines represent clocking signals, and dashed lines represent trigger signals.

The delay generator also triggers the solid state amplifier to amplify the signal for only the duration of the input pulse.

The detection electronics include a high-gain, low-noise amplifier (Miteq AMF-5F-08001800-14-10P), a mixer to downconvert the double-sideband signals (Marki MIR0726), and an Agilent digital-to-analog converter (DAC) board. This DAC board is clocked to the same external source as the DDS board, and samples the molecular FID at 4 GS/s. FID collection is triggered by the DDS board, and up to 10 million FIDs are averaged at a time before being written directly to text files. Critically, both the DDS board and the DAC board have low latency. This ensures high duty cycles even under continuous excitation and FID acquisition environments.

The system is clocked by a rubidium frequency standard (Stanford Research Systems Model FS725 Rubidium Frequency Standard), providing a time base for a Valon dual frequency synthesizer (Valon Technology LLC 5008) that is used as a reference for the DDS board and the digitizer. The rubidium standard also clocks the LO signal generator to ensure phase stability.

We have tested both pinhole and slit expansions. There is some concern about collisional broadening for the latter, as the pressure at the outlet of the slit decreases more slowly than in pinhole expansions, and because such collisions are clearly manifest in pulsed large aperture Laval nozzle expansions (Oldham et al., 2014) used to study low temperature chemical kinetics. To confirm that the mach disk for the slit nozzle is sufficiently far from the slit, experiments with longer FID acquisitions were run. Normally, an FID of 18 microseconds is taken, as this maximizes the signal-to-noise ratio of the observed peaks in a given wall clock time. Longer FIDs optimize the spectral resolution, at the cost of reduced sensitivity.

To characterize the expansions, experiments with molecular FIDs of 50 microseconds were acquired for both the slit and point source nozzle. With Ar as the carrier gas (used for its rotational cooling (Campbell et al., 1981) and cluster generation efficiency) at 0.4 atm background pressure, a mixture of argon and ethanol was flowed continuously into the chamber at 50 sccm. Under these conditions, the pressure in the chamber hovered near $2.0 * 10^{-4}$ torr. With a 12.0 GHz LO field and 50 million averages collected, the full width half max (FWHM) of the strongest peaks was

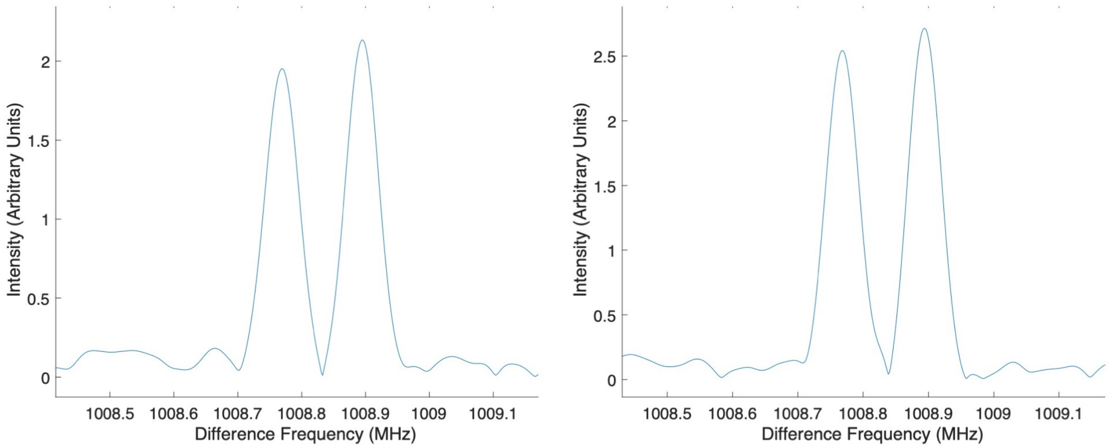

Figure 2.4: Long FID (50 microsecond) collection for 1 mm diameter circular source (left) and a 10 cm × 25 μm slit nozzle (right) continuous expansions of Ethanol at 0.4 atm, 50 sccm flow. Longer FIDs result in resolution of the Doppler splitting of the ethanol dimer line at 1008 MHz offset from the 12.0 GHz LO frequency. Full width half max of each line is 60 KHz.

~60 kHz for both the point source and the slit expansion, as shown in Figure 2.4. These longer FIDs also reveal the expected Doppler splitting of transitions, a result of the emitted radiation propagating both towards the horn and away from it, then reflecting back in to the detection circuit.

The consistent width of the peaks for both the point source and slit nozzle expansions indicates that collisional broadening is not significant for either nozzle under these expansion conditions. At carrier gas background pressures exceeding 1 atm, initial experiments do show that the peaks from the slit nozzle are slightly wider than those from the point source nozzle, implying that this is the maximum background pressure for a slit nozzle continuous expansion to avoid collisional broadening of the pure rotational transitions of molecules and clusters in the molecular beam.

2.3 Results and Discussion

Computational results

To aid in spectral assignments, *ab initio* calculations for the equilibrium and ground state rotational constants were carried out with second order Møller-Plesset (MP2) perturbation theory using the 6-311++G(d,p) basis set with anharmonic corrections via the Gaussian 09 package (Frisch et al., n.d.). This level of theory and basis set choice have previously been used in studies of the ethanol/water dimer, and produce reasonably accurate rotational constants without taking prohibitively long to converge on modest clusters (Finneran, Carroll, et al., 2015). Initial structures were generated based on chemical intuition and from comparison to studies in the literature (Malloum, Fifen, and Conradie, 2020; Finneran, Carroll, et al., 2015). Images of the lowest energy structures for $(C_2H_5OH)_2H_2O$ are shown in Figure 2.5. The rotational constants from the converged structures were used to simulate spectra with the program PGOPHER (Western, 2017). These rotational constants are shown in the first column of Table 2.1 for the two lowest energy conformers of the ethanol trimer, and in Table 2.2 for the lowest energy conformers of the trimer formed between two ethanol molecules and one water molecule. Observed rotational lines were then fitted with the program SPFIT (Pickett, 1991), and the fitted rotational constants were compared to the *ab initio* results.

As expected from water cluster studies, the main motif of the trimers involves a cyclic pattern where all monomers accept and donate hydrogen bonds. The more subtle structures of interest here are conformers related to the orientation of the carbon groups with respect to the plane of hydrogen bonding. All spectra are rigid-rotor like, and it is not the goal of this work to capture modes associated with internal rotation. In addition, the height of barriers between conformers is not empirically derived.

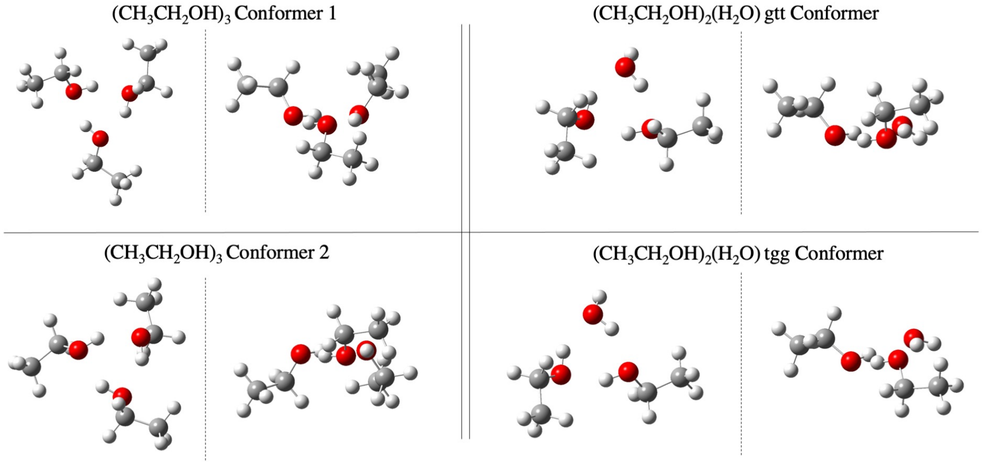

Figure 2.5: The two lowest conformations for the pure ethanol trimers and those with two ethanol and one water monomer. The top row is the lowest energy conformation, that for the bottom row lies <1 kcal/mol higher in energy. Optimized structures and rotational constants were determined via Gaussian 16 at the MP2 level of theory and 6311+G(d,p) basis set. The left column shows a 'top-down' view of the hydrogen bonding in the conformers, and the right column shows a 'side' view with respect to the hydrogen bonded cyclic motif, emphasizing the difference configuration of the ethanol carbon chains.

The *ab initio* energy difference between the two lowest energy conformers of both the pure ethanol and the mixed trimers is <1 kcal/mol, and suggested that both conformers should be observable in experimental spectra. The ethanol subunits of both pure ethanol trimers and mixed trimers are all in the trans configuration in the isolated structures. However, as seen in Figure 2.5, the orientation of the ethanol molecules relative to the plane of hydrogen bonding interactions varies between the conformations– the mixed ethanol and water trimers are shown as an example. In the top row, this conformer has a gauche relationship between the ethanol groups, and both ethanol molecules are trans to the water molecule. In contrast, the bottom row shows a conformer that is trans between the ethanol groups, and gauche relative to the water. The first mixed trimer configuration shown is referred to in this paper as “gtt", and the second is referred to as “tgg".

The two lowest energy structures calculated for the pure ethanol trimer both have two trans relationships between the ethyl groups, and one gauche. The lowest energy structure is labeled as Conformer 1, and the second lowest is labeled as Conformer 2. The energy difference between these structures is less than 1 kcal/mol. The lack of gauche conformation ethanol in all identified trimers implies that the stability afforded by additional hydrogen bonding interactions is less than the energy cost of overlapping ethanol groups. Further study of neat and mixed water:ethanol trimer isotopologues would help elucidate this trend.

Experimental results

Experimental spectra were recorded for pure ethanol and for a mixed expansion of ethanol and water. Experiments with 0.7 atm background pressure of argon, 50 sccm gas flow, and an 18 microsecond FID collection time achieved a signal-to-noise (S/N) ratio of 830:1 for lines assigned to the ethanol trimer, with a full width half max (FWHM) of 100 kHz. For the mixed trimers, the S/N ratio was ~80:1 for the strongest identified lines, with the same FWHM as the ethanol trimer lines. Spectra collected under these conditions with LO settings of 11.6 to 12.1 GHz and from

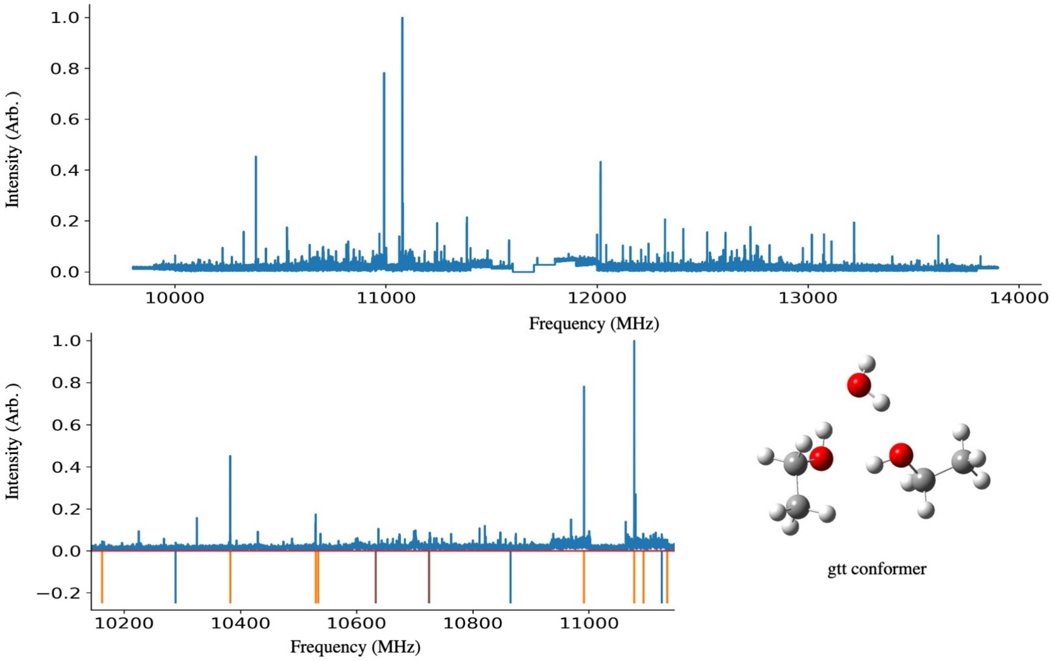

Figure 2.6: Example of the experimental spectra collected on the mixed expansion of water and ethanol. On top is the full bandwidth collected, the bottom spectrum shows an inset of this spectrum with lines fitted for pure ethanol monomer (orange), water monomer (red), ethanol/water dimer (green), ethanol trimer (brown), and the mixed trimer of the up/down configuration (blue). The full spectrum is 200 million averages each of 6 LO settings, corresponding to approximately 13 hours of data collection. To right is the gtt conformer for reference.

17.5 to 17.6 GHz were compared with the spectrum generated from the *ab initio* calculated rotational constants using PGOPHER for line assignment. Data sets were processed by removing known lines of the ethanol monomer, water monomer, and pure and mixed dimers of each from the spectrum. The spectroscopic accuracy and precision, and FWHM trends, were bench marked by comparison to known lines of the ethanol monomer, values for which were obtained from the JPL Molecular Spectroscopy Database (Pickett et al., 1998), and are commensurate with previous experimentation in the Blake lab, as described in the methods.

Table 2.1: Computational and experimentally determined rotational constants for the lowest energy conformer (conf.) of the ethanol trimer. Parameters are fitted *via* SPFIT, using Watson's reduction of the Hamiltonian. N is the number of lines from the experimental spectrum fit, and the values in parentheses are the 1σ errors reported by SPFIT.

	Ab initio Conf. 1	Fitted Conf. 1	*Ab initio* Conf. 2	Fitted Conf. 2
A/MHz	995.9	996.29 (4)	1015.8	1012.48 (4)
B/MHz	801.9	802.64 (10)	798.5	800.36 (22)
C/MHz	469.4	469.31 (21)	473.9	474.28 (18)
D_J/kHz	2.88	15.12 (9)	2.44	-1.31 (17)
D_{JK}/kHz	-6.87	-47.6 (3)	-5.28	-35.53 (6)
D_K/kHz	4.21	36.42 (24)	3.04	41.17 (6)
d_1/kHz	1.01	4.54 (4)	0.841	13.78 (16)
d_2/kHz	-4.48	37.77 (24)	-2.65	77.10 (10)
μ_a/D	1.18		1.22	
μ_b/D	-0.30		-0.28	
μ_c/D	-0.14		0.17	
N		12		13
rms/kHz		56		96

Lines observed in the spectrum were then fitted with SPFIT to generate calculated rotational constants, shown in Table 2.1 for the ethanol trimer and Table 2.2 for the mixed trimers. The trimers of interest are locked in a circular H-bond motif, meaning that the current work focuses on distinguishing between various conformations of this locked H-bond motif, as opposed to different bonding structures.

By comparison to these spectra simulated with PGOPHER, the rotational temperature of the clusters was estimated to be 10 K. At this temperature, there were between 15 to 30 strong rotational lines in the spectral range of the experiment for each type of cluster. At least half of the strong lines expected to be observed were fit to calculate the rotational constants from experimental spectra. Specifically, 12/25 lines were fit for conformer 1, and 13/20 lines were fit for conformer 2 of the pure ethanol trimers. For the mixed trimers, 10/20 lines were fit for tgg, and 9/20 lines were fit for gtt.

Of these lines fit for each trimer, most were *a-type* rotational transitions, as expected from the relative magnitude of the A, B, and C rotational constants and the electric dipole projections. First, these *a-type* transitions were fit. Next, at least one *b-type* and *c-type* transition were fit for each trimer to help improve the fit of the experimental constants. To more accurately assign these weaker *c-type* transitions, the chirp bandwidth was reduced to 1 GHz, enhancing the molecular polarization, and thus FID intensity, with the available amplifier output. This increased power density was essential in assigning the lower intensity *c-type* transitions, for which only the strongest predicted transitions were sought for, and fit, with relative intensity of 70% of the *a-type* spectral lines. All key transition assignments were verified with dual resonance experiments.

Rigid rotor fit r.m.s. values were higher than previous work, at $\sim$100 kHz, which is mostly likely explained by internal rotations of the methyl subgroups splitting the observed rotational transitions. The barrier to rotation for these methyl subgroups was calculated to be $\sim$1100 cm^{-1} using *ab initio* techniques with Gaussian. As seen in previous work, coupling to large amplitude motion of the trimer will effectively lower the barrier to internal rotation of the methyl groups, which would result in increased internal rotation splittings, and result in increased r.m.s. to the overall fits since in this case the pure all A-state combinations of the tops cannot be separated from mixed A-E and E-E states (Khemissi, Salvador, and Nguyen, 2021; Ferres et al., 2019; Mélan, Khemissi, and Nguyen, 2021).

To assess the likely size and nature of the line splittings associated with the modest barriers to internal rotation, the trimer spectra were modeled with the internal rotation fitting program XIAM (Hartwig and Dreizler, 1996). The results indicate that for rotational mode splittings of up to 100 kHz, approximately the largest residuals in the rigid rotor fits, to lines most susceptible to internal rotation perturbations, a barrier to internal rotation of approximately 1000 cm^{-1} is needed. Thus, the magnitude of the barrier is only modestly lowered by coupling to the other large amplitude motions of the cluster, as expected due to the interlocked donor-acceptor nature of the trimers. In addition, the sign of the error between the SPFIT model and XIAM agrees, supporting the plausibility of the internal rotation fitting.

This magnitude of splitting is too small to be resolved, even with longer FID collection (~50 microseconds), with the present instrument, although the asymmetry in both peak shape and relative intensity of doppler splitting observed in the line shapes of these long FID experiments supports this magnitude of splitting due to internal rotation. Quantitative studies of these splittings would require a large cavity, coaxial geometry Flygare machine, and is beyond the scope of the present work. Simple order-of-magnitude estimates of the offsets of the A symmetry transitions from the peaks of the internal rotation envelopes with the current instrument lower the fit r.m.s. by factors of 2-3, as discussed in the Supplementary Information, included in Appendix A.

Importantly, this increased error does not influence the line assignment; the various conformers observed have larger spectral differences than the r.m.s. error of the fits, and the lines included in these fits have been verified with dual resonance experiments. Thus, we are confident in the assignment of lines to different conformers and the geometric differences of these conformers that give rise to the spectral variation observed. This demonstrates the improvement in sensitivity of the current instrument over previous work, and opens the door for further projects investigating conformational variation in high order clusters.

As discussed in the experimental section, the most impactful change in this system was the integration of a high speed, high compression ratio turbomolecular pump into the experimental chamber, coupled to high speed/high duty cycle digital electronics. Compared to previous CPFTMW experimentation, this single change increased the duty cycle of the system from ∼1% to upwards of 70%, thanks to the new capability to introduce gas continuously into the chamber without overloading the pumps, and with no pressure broadening of the rotational spectra due to the low background pressure enabled by the uniquely high compression ratios achieved with high throughput turbomolecular pumps. The higher duty cycle resulting from continuous expansion thus led to decreased lab time required for experimentation, altogether speeding up the data collection process. The signal to noise ratio of 830:1 achieved here for the ethanol trimers was the result of 13 hours of averaging;

the former incarnation of this instrument achieved a signal to noise ratio of ~200:1 on the peaks of interest after 40 hours of averaging (Finneran, Good, et al., 2015; Finneran, Holland, et al., 2013). Thus, though a modest technological innovation, the increased pumping speed has dramatic impact on the speed and ease of experimentation. In addition, the implementation of continuous throughput high duty cycle experiments combined with a slit expansion geometry have allowed for novel clusters to be identified. Importantly, the slower fall off in beam density enables improved cluster generation efficiencies, especially for higher order clusters. For example, with an SNR of more than 100:1 for water hexamer lines, compared to a previous SNR of 15:1 in the same wall clock time, the high pumping speed and low background enabled by the turbomolecular pump provides an optimal environment for the rotational study of clusters, where large interaction volumes are pivotal.

This arises because under similar expansion and excitation conditions, the sensitivity of a chirp pulse instrument depends on the noise figure of the detection circuit and the number of FIDs averaged. For a given instrumental noise figure and chirp bandwidth, because the turbopump enables continuous expansions to be run, at least for dimers and trimers, under conditions that match cluster generation efficiency in pulsed operation, no sensitivity is lost with high duty cycle DAC systems. That is, there is no difference in the number of microwave pulses needed to achieve a given S/N, but the time required to achieve it is decreased by the increased sample consumption per unit wall clock time. With commercially available high power amplifiers and multi-card DAC systems analog bandwidths of >10 GHz can be acquired and averaged on the fly. Thus, on balance, it is the view of the authors that the increased rate of material consumption per unit time does not necessarily imply high sample consumption rates, and with sufficiently high bandwidth DAC systems is entirely consistent with isotopically enriched sample studies for structural determination. This conclusion may not be valid for large clusters of low volatility species, which will likely require stringent, very high pressure expansion conditions, but should true for a very wide range of substances of chemical interest. And, the improved clustering efficiency of the slit expansion leads to good sensitivity to larger clusters. For example, with the current system, methanol and methanol-water clusters up to the hexamers are readily seen, as will be described in future publications.

Table 2.2: Calculated and experimentally determined rotational constants for the mixed water and ethanol trimers observed. Parameters are fitted *via* SPFIT, using Watson's reduction of the Hamiltonian. N is the number of lines from the experimental spectrum fit, and the values in parentheses are the 1σ errors reported by SPFIT.

	Ab initio tgg	Fitted tgg	*Ab initio* gtt	Fitted gtt
A/MHz	2711.4	2709.38 (7)	2414.6	2406.62 (3)
B/MHz	922.7	923.47(17)	1069.7	1068.14 (7)
C/MHz	724.6	724.86 (13)	809.9	810.01 (16)
D_J/kHz	0.79	-20.9 (9)	2.69	-151.7 (6)
D_{JK}/kHz	-0.71	54.2 (26)	-6.55	289.1 (13)
D_K/kHz	18.22	-31.1 (17)	14.27	-135.9 (6)
d_1/kHz	0.19	14.1 (5)	0.67	58.70 (26)
d_2/kHz	2.56	-22.4 (12)	3.37	-29.81 (21)
μ_a/D	0.69		1.17	
μ_b/D	-0.48		-0.41	
μ_c/D	0.073		0.14	
N		10		9
rms/kHz		117		82

2.4 Conclusions

The observed ethanol trimer and mixed ethanol and water rotational spectra demonstrate the effectiveness of *ab initio* calculations for predicting structures and rotational constants of this class of small molecule clusters. The computed and fitted rotational constants are relatively close in value, reflecting the accuracy of the *ab initio* methods. This accuracy is consistent with the rigid structure of the hydrogen bonding ring in these trimers; the stability afforded by the uniform hydrogen bond donor and acceptor configuration ‘locks’ the geometry into conformation, making the potential energy surface of these trimers steeper between conformers and allowing calculational methods to more easily, and accurately, predict structural parameters.

This work has also served to demonstrate the efficacy of this new instrument for rotational studies of small molecule clusters. The high throughput afforded by the increased pumping speed of the turbomolecular pump decreases the lab time required for experimentation by a factor of ten over previous instruments, and the high compression ratio enables modest backing pumps and roughing lines to be used. This efficiency expands the scope of potential research targets, as demonstrated herein with the identification of mixed water:ethanol trimers in a dense rotational spectrum. Future work in this area will benefit from the speed of data collection with continuous expansion, and will work to identify similarly difficult to isolate small molecule clusters.

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Chapter 3

STUDY OF ETHANOL AND WATER TETRAMERS

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3.1 Introduction

From protein solvation to aqueous geochemistry, a vast array of modeling relies on accurately constraining the interactions of few water molecules at a time (Keutsch and Saykally, 2001; Bosma, Fried, and Mukamel, 1993; Fellers, 1999; Smith et al., 1990; Cole et al., 2015). This few-atom computational problem is non-trivial however, as the network of hydrogen bonding defining the intermolecular potential energy surface of water is complex, and traditionally difficult to study.

Recent advances in coherent, broadband microwave and terahertz generation and spectroscopic technologies have opened the door for more detailed studies of water on the micro-scale (Jarrahi, 2015; Yardimci et al., 2017). As these questions begin to be answered, more arise as to how this hydrogen bond network of water aggregation is disrupted by other small molecule hydrogen bond donors and acceptors, such as low molecular weight alcohols. Understanding alcohol:water mixing at a few-molecule scale carries weight for understanding the bulk properties, and the anomalous negative entropy of mixing characteristic of these substances (Juurinen et al., 2011; Soper et al., 2005; Calabrese et al., 2021), for understanding solvation effects for reactions conducted in alcohol:water solvents (Neeman and Huet, 2021; Lenton et al., 2018), and even for the physicochemical and antiviral/antibacterial properties of hand sanitizer (Nyamweya and Abuga, 2021; Abuga and Nyamweya, 2021), particularly relevant during this period of heightened demand.

As shown in the previous chapter, instrumentation development in the Blake group has allowed for studies of trimer clusters, and in addition, the novel capabilities of the high throughput system allow for the study of larger and more complex clusters. This progressive study of higher molecular weight clusters can thus eventually inform bulk studies of alcohol and water mixtures, as well as providing insight into the variations in behavior between neat alcohol and water clusters on the small scale.

To begin building an understanding of the local environment of water:alcohol mixing, a precise potential energy surface of few molecule interactions is required. The best tool to start mapping this small cluster energy landscape is again chirped pulse Fourier-transform microwave spectroscopy (Brown et al., 2008; Mead et al., 2017; Juanes et al., 2019; Donatella Loru, Isabel Peña, and M. E. Sanz, 2019). By yielding experimentally determined rotational constants, this technique provides an atomically-accurate geometry of small molecule clusters of interest, showing the bonding pattern and determining which out of multiple minima on the potential energy surface for a potential cluster are physically observed. In addition, the high spectral resolution of this technique allows for fitting of split rotational states due to internal rotation or tunneling, not just the vibrationally averaged minimum geometry.

In the this chapter, pure ethanol and water:ethanol tetramers are targeted, in an effort to understand the asymmetric geometry that allows for a net dipole in these clusters, and to elucidate the patterns of micro-aggregation of water and ethanol vs. the homogeneous distribution of these species throughout the tetramer. Multiple conformers of most tetramers are observed, and confirmed through isotopic substitution. In addition, splitting and line center displacements in the rotational spectra due to internal rotation of the methyl groups in ethanol are investigated (Khemissi, Salvador, and Nguyen, 2021; Ferres et al., 2019), and estimated computationally.

3.2 Experimental

Following the work of Mejía et al (Mejía, Espinal, and Mondragón, 2009), the lowest energy structures of the pure ethanol and mixed water:ethanol tetramers were optimized with Gaussian 16 (Frisch et al., n.d.). Local minima were identified, and anharmonic corrections to rotational constants were retrieved using the DFT method at the B3LYP level of theory and the 6311g++G(d,p) basis set. Previous work had shown that this level of theory and basis set were sufficient for calculating approximate rotational constants (Finneran et al., 2013; Mejía, Espinal, and Mondragón, 2009; Mead et al., 2017). Relative energies of all the calculated conformers of ethanol:water tetramers are shown in the Supplementary Information in Appendix B, where a trend of increasing energy with increased water content in the tetramers is evident.

As expected from the cyclic water tetramer, all cluster conformers are based on a motif where the ethanol and water monomers act as both a hydrogen bond donor and acceptor. To further refine the cluster geometries, experimental spectra were collected using the Blake Group high throughput CPFTMW apparatus described previously (Dutton and Blake, 2022). Clusters were formed by bubbling argon through solely ethanol or separate flasks of ethanol and water at a backing pressure of 1.5 atm, with the water flask heated to approximately 60 °C to form clusters with higher water content. The gas stream was expanded continuously through a 10 cm $\times$ 25 μm slit nozzle into the vacuum chamber, and the background pressure was kept below $4 * 10^{-4}$ torr during the continuous expansion. After each excitation pulse, free induction decays (FIDs) of 18 microseconds were collected, and 200 million were averaged together at a time for each local oscillator (LO) setting. This corresponded to a wall clock experiment time of just over 2 hours for each LO setting. The signal-to-noise ratio for the monomer lines observed was on the order of 3000:1, and for the tetramer lines detected, it was on the order of 10:1. A sample of the experimental spectra collected, with assigned lines, is shown in Figure 3.1.

For the pure ethanol tetramer, there were three lowest energy conformers identified in previous work, denoted 2g-2g+, 2g-g+t, and 2tg+g-. Depictions of these conformers and their relative energies are shown in Figure 3.2. Of these conformers, only the 2tg+g- conformer had a dipole moment of sufficient strength, that is, above 0.4 debye, to be seen via chirped pulse rotational spectra with the available microwave peak power. This conformer was the highest in energy out of the computed minima

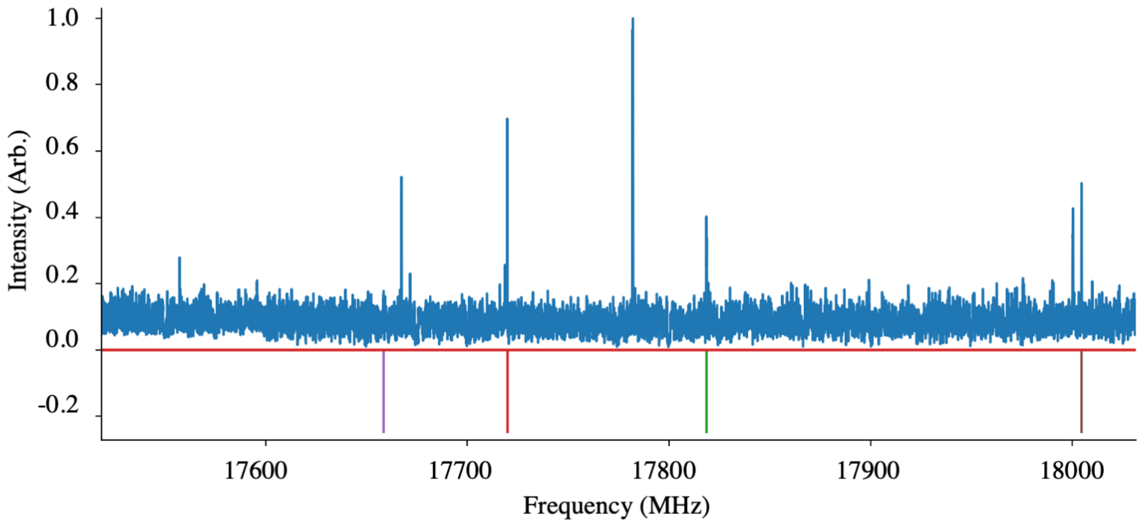

Figure 3.1: Section of experimental spectrum with lines fit for various EtOH-water tetramer species. Pictured are lines fit to the $(H_2O)_2(C_2H_5OH)_2$ wg1tw (green)/wttw (red) and $(H_2O)(C_2H_5OH)_3$ wg1g2t (purple)/wttt (brown) tetramers

.

structures, however the difference in energy between the conformers, around 0.1 kcal/mol, was small enough that we would expect to see all conformers forming in the supersonic expansion. Previous work studying the dimerization of ethanol has shown a similar trend in the supersonic expansion experimental signatures of conformers with similar energy, in which all of these low-energy conformers were identified (D. Loru, I. Peña, and M. Sanz, 2017). This work therefore supports the conclusion that all low-lying conformers with sufficiently large dipole moments should be observable in the expansion.

Of the 30 conformers of $(H_2O)(CH_3CH_2OH)_3$ clusters reported previously, the lowest nine in energy were minimized in Gaussian. Of those, many are highly symmetric, leading to a low dipole moment and therefore experimental challenges to observe the structures in rotational spectra. Altogether, two of these eight most

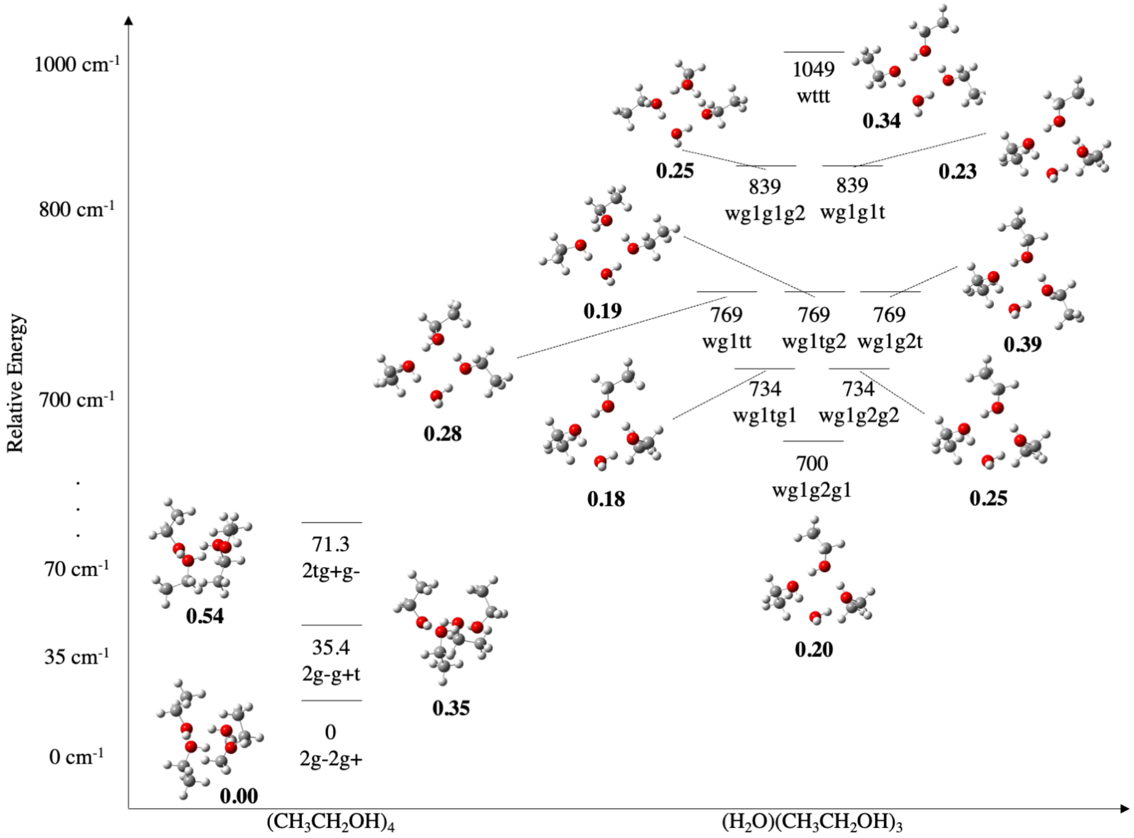

Figure 3.2: Relative energies of the lowest three conformers of the pure ethanol tetramer and lowest nine conformers of $(H_2O)(CH_3CH_2OH)_3$. Dipole moments (in debyes) listed below the figure of each conformer. Jump in energy corresponds to difference in tetramerization energies of $(CH_3CH_2OH)_4$ and $(H_2O)(CH_3CH_2OH)_3$ from the literature (Mejía, Espinal, and Mondragón, 2009).

stable conformers have net dipole moments about 0.3 debye, and were identified in experimental spectra. These structures are denoted wttt and wg1g2t, according to the relative conformation of the ethanol subunits; wttt has all trans ethanol, wg1g2t has two gauche ethanol molecules, on opposite sides of the plane of hydrogen bonding, and one trans molecule. Figure 3.2 shows that while these two conformers are not the lowest in energy of all the conformers with one water calculated, they are the only conformers with a large enough dipole moments. Thus, while other conformers of $(H_2O)(CH_3CH_2OH)_3$ are lower in energy, and likely formed during the expansion of water and ethanol, they are not detectable in the spectra collected.

Similarly, two conformers of $(H_2O)_2(CH_3CH_2OH)_2$ clusters were observed in the spectra. Previous computational work has not included a full survey of these clusters, so the cyclic forms of these clusters were optimized by building on the work of Mejía et al. and substituting an additional water molecule into the cyclic mixed tetramer structures. Every variation of gauche and trans geometry for the ethanol molecules was combined with every variation of relative position around the ring of hydrogen bonding. It was observed that these structures were all very close in energy, spanning under 0.1 kcal/mol in total. In addition, of these structures, few had dipole moments sufficient to give an observed signal experimentally, similarly to the one water clusters. The two conformers with sufficiently high dipoles were those denoted wg1tw and wttw, one with both ethanol groups in trans conformations, and another with one trans ethanol and one gauche.

Finally, the $(H_2O)_3(CH_3CH_2OH)$ cluster was studied; two conformations of the structure with circular hydrogen bonding are present, corresponding to the two conformers of ethanol. These two different conformers of the three-water cluster are again close in energy, and each has a low net dipole. By increasing backing pressure of the Argon carrier gas to 2 atm, and increasing temperature of the water sample to approximately 60 °C, production of these tetramers was optimized, and both conformers were identified in the spectra. These are referred to as twww and gwww, referring to the trans configuration of the ethanol sub-unit vs. the gauche, as can be seen in Figure 3.3.

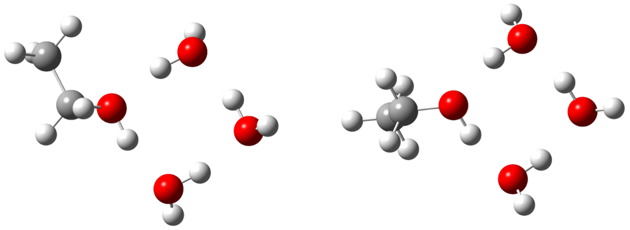

Figure 3.3: Comparison of gauche and trans geometry between $(H_2O)_3(CH_3CH_2OH)$ conformers.

3.3 Results

The implementation of CPFTMW used to target ethanol and ethanol:water clusters described above yielded spectra spanning 10 to 18 GHz, with signal to noise ratios on the lines of interest of $\geq$10:1. From these spectra, a, b and c type transitions were fit for all observed conformers, with a-type transitions most abundantly observed, consistent with this being the strongest dipole moment component of the tetramers. These transitions correspond to J values ranging from around 10 to 20 for higher ethanol content clusters, and 5 to 10 for higher water content clusters.

To confirm individual line assignments, dual resonance experiments were conducted on the strongest lines observed for each conformer. This allowed for definitive assessment of how the rotational states observed related to each other, supporting the correct assignment of quantum states. With these appropriately assigned lines, experimental rotational constants were retrieved using the program SPFIT (Pickett et al., 1998). Comparisons of calculated rotational constants and anharmonic correction terms to experimentally determined values are shown in Table 3.1 for the pure ethanol tetramer conformers, Table 3.2 for the $(H_2O)(CH_3CH_2OH)_3$ conformers, Table 3.3 for the $(H_2O)_2(CH_3CH_2OH)_2$ conformers, and Table 3.4 for the $(H_2O)_3(CH_3CH_2OH)$ conformers. Distortion constants were fit with SPFIT, but omitted from final fits with a low number of lines available in the spectra. The robusticity of the fits for A, B, and C rotational constants is such that geometry of the clusters can be predicted to high precision, and are in good agreement with the calculated rotational constants.

Experimental line strengths indicate a rotational temperature of ~10 K when compared with simulated spectra. Populations among cluster types are less straightforward to estimate, given weak lines and highly dense spectra observed, but from comparing line strengths in fairly narrow spectral windows and transitions with similar predicted intensities, we see that relative ratios of conformers vary from 1:1 to 5:1. When these ratios are scaled with respect to the predicted energy differences between the conformers, there is no clear trend that could be used to estimate a vibrational temperature that could explain the relatives populations among cluster types. This may be due to the fact that many conformers of each tetramer are undetectable with the current instrument, given their low dipole moment projections. What does seem to follow is that when there are fewer available conformers in a certain cluster type, i.e., only two available conformers (twww and gwww) for the three water tetramer, the relative populations (when corrected for the different predicted dipole moments) are noticeably different, close to a 5:1 ratio that favors the lower energy cluster. For the cases where more cluster geometries are close in energy, such as one water and two water tetramers, the relative populations are more even, indicating a more stochastic distribution between the accessible conformers. Taken together, the results do imply a somewhat higher vibrational (or conformer) temperature than rotational excitation temperature within a given cluster. This is consistent with previous pinhole expansion experiments, but the difference is perhaps smaller (as demonstrated by the three water cluster populations), and likely due to the more extensive soft collisional environment afforded by a slit nozzle.

To additionally confirm conformer assignment, isotopically enriched samples were used to experimentally compare hydrogen positions within the observed tetramer conformers. From these deuterated sample experiments, isotopologues of each conformer were observed in the spectra, confirming assignment of every conformer reported herein. Figure 3.4 shows the substituted geometry compared to the assigned conformer hydrogen position for two conformers as an example. In addition, hydrogen exchange during sample preparation or data acquisition with D_2O led to the formation of HDO as well, thus allowing for tetramer clusters to form with single isotopic substitution in the water subunits. These singly substituted species for each conformer were fit, and Kraitchman analysis performed to calculate H position for a donated H from a water molecule (Kisiel, 2001). Singly deuterated ethanol was also formed during hydrogen exchanged, but these isotopologues were not fit due to low abundance. For further details on experimentally fitting these isotopologues, see the Supplementary Information in Appendix B. The results of the perdeutero fits provide additional data as to the the accuracy of modeled rotational constants with fit rotational constants, in addition to qualitatively confirming the correct conformer assignment of the observed tetramers. To further confirm these conformer assignments and geometries, the results from the singly deuterated isotologues allow us to quantitatively calculate the hydrogen position via the Kraitchman equations.

When fitting some transitions for the tetramer species observed, higher error than experimental precision was observed, especially for transitions from high J states. This higher error can be explained by the internal rotation of the methyl groups present in these clusters, which splits the rotational transitions observed. The magnitude of this splitting is directly proportional to the height of the barrier to methyl group rotation. For the ethanol monomer this barrier is $\sim$1185 cm^{-1} for the trans conformer $\sim$1250 cm^{-1} for the gauche conformer (Durig and Larsen, 1990). This high of a barrier leads to a low magnitude of splitting of the rotational states, up to a few tens of kilohertz.

To model the splitting of rotational states in mixed ethanol and water tetramers due to internal rotation, the program XIAM (Hartwig and Dreizler, 1996) was used. This program works well to model splitting from up to two internal rotors, thus tetramers with additional rotors were simplified by assuming that rotors with similar local environments and similar geometry within a conformer could be approximated to be the same type of rotor. The output of XIAM is therefore an approximation, as the geometry inputs do not reflect all the internal rotation possible in some of the tetramers. This is sufficient however, as we are more interested in the magnitude of the splitting of rotational states than the absolute line positions.

The magnitude of this splitting of rotational states due to internal rotation was thus determined to be on the order of 10 kHz, which supports the increased error we see in line assignment. This low-level splitting is too small for us to resolve with our instrumentation however; higher resolution could be achieved with the use of a large cavity, coaxial Flygare instrument.

The results of these isotopologue fits show good agreement between calculated rotational constants and fitted rotational constants, thus implying that the modeled geometries are good approximations of the true vibrationally averaged structures. From the conformers observed in experimental data, a trend appears in calculated average O-O bond distance. This distance increases for mixed tetramers, but as progressively more water is incorporated into the ethanol tetramers, average O-O bond distance decreases. For pure ethanol tetramers, this distance is on average 2.71 to 2.72 Angstroms, depending on the conformer. For $(H_2O)(CH_3CH_2OH)_3$ tetramers, this average distance is around to 2.75 Angstroms, then is essentially the same at 2.74 for $(H_2O)_3(CH_3CH_2OH)$ clusters. This same pattern is observed for trimers; O-O distance is increased in mixed trimers. For full details, see Supplementary Information, included in Appendix B.

This trend in O-O distance speaks to the strength of hydrogen bonds in these pure and mixed clusters. The increase in distance implies a weakening of interaction strength between water and ethanol, then a successive increase in hydrogen bonding strength as more water is substituted into the clusters. This may be explained by the higher cooperativity available to water, given the multiple hydrogen bond acceptor and donor sites on water. This potential for higher cooperativity allows for water to bond in more compact, three dimensional geometric patterns as cluster size increases, as seen in previous work (Pal, Patla, and Subramanian, 2021; Sun and Schnell, 2022; C. Pérez, Lobsiger, et al., 2013; Maeda and Ohno, 2007; C. Pérez, Muckle, et al., 2012; C. Pérez, Zaleski, et al., 2014). This cooperativity is limited in pure ethanol clusters, and in addition, the steric hindrance of the carbon chain further weakens the hydrogen bonding interaction in mixed water:ethanol tetramers. Of note, then, is the implied greater strength of hydrogen bonding in pure ethanol tetramers from the shorter O-O bond distance, which is also supported by the lower energy of pure ethanol tetramers as shown in Figure 3.2. In comparing these O-O bond distances with previous work on clusters with net cooperativity of 2, the conclusion of tighter binding in these tetramers is supported; for example, in pure water decamers with cooperativity=2, the average O-O distance is between 2.74 and 2.80 (C. Pérez, Zaleski, et al., 2014), and in pure water tetramers, this average O-O distance ranges from 2.74 (J. F. Pérez, Hadad, and Restrepo, 2008) to 2.85 Angstroms (Ludwig, 2001) depending on the conformer.

With this result, future work investigating the diverse range of 3-dimensional structures in mixed alcohol-water clusters of increasing size may further elucidate the pattern seen here in the O-O distance of mixed ethanol-water tetramers, in which each monomer serves as both a hydrogen bond acceptor and donor.

Table 3.1: Calculated and experimental rotational constants of $(CH_3CH_2OH)_4$ conformers identified in spectra.

	2tg+g- DFT	Fitted 2tg+g-
Dipole	0.54	
μ_A	0.44	
μ_B	-0.28	
μ_C	-0.15	
A (MHz)	550.2	550.83 (6)
B (MHz)	530.9	539.16 (22)
C (MHz)	464.6	464.68(13)
D_J (kHz)	0.53	12.30 (23)
D_{JK} (kHz)	-0.32	-39.44 (5)
D_K (kHz)	0.11	27.74 (22)
d_1 (kHz)	.09	9.69 (8)
d_2 (kHz)	-0.15	-26.68 (16)
Error (kHz)		87
N		14

Table 3.2: Calculated and experimental rotational constants of $(H_2O)(CH_3CH_2OH)_3$ conformers identified in spectra.

	wttt DFT	Fitted wttt	wg1g2t DFT	Fitted wg1g2t
Dipole	0.34		0.39	
μ_A	-0.25		-0.39	
μ_B	0.22		-0.05	
μ_C	-0.07		-0.05	
A (MHz)	981.9	982.11 (3)	1038.9	1036.86 (16)
B (MHz)	530.0	528.58 (17)	538.6	538.36 (5)
C (MHz)	355.1	355.20 (10)	382.4	381.67 (17)
D_J (kHz)	0.46	5.74 (5)	0.22	2.14 (8)
D_{JK} (kHz)	-0.84	-28.60 (5)	-0.30	-190.4 (4)
D_K (kHz)	0.42	23.70 (4)	1.26	188.3 (3)
d_1 (kHz)	0.15	1.34 (17)	0.67	24.52 (24)
d_2 (kHz)	-0.17	12.63 (30)	1.78	98.23 (16)
Error (kHz)		33		25
N		13		10

Table 3.3: Calculated and experimental rotational constants of $(H_2O)_2(CH_3CH_2OH)_2$ conformers identified in spectra.

	wg1tw DFT	Fitted wg1tw	wttw DFT	Fitted wttw
Dipole	0.48		0.52	
μ_A	-0.47		-0.48	
μ_B	-0.09		-0.17	
μ_C	-0.05		0.14	
A (MHz)	1460.0	1458.78 (4)	1305.3	1305.26 (6)
B (MHz)	830.5	832.49 (24)	897.7	897.68 (8)
C (MHz)	586.7	587.02 (17)	552.9	552.91 (24)
D_J (kHz)	0.70	30.30 (21)	1.06	–
D_{JK} (kHz)	1.16	-88.40 (70)	-2.06	–
D_K (kHz)	-0.30	57.00 (5)	1.11	–
d_1 (kHz)	0.17	6.17 (12)	0.070	–
d_2 (kHz)	1.35	9.90 (13)	-0.44	–
Error (kHz)		74		96
N		12		10

Table 3.4: Calculated and experimental rotational constants of $(H_2O)_3(CH_3CH_2OH)$ conformers identified in spectra.

	twww DFT	Fitted twww	gwww DFT	Fitted gwww
Dipole	0.29		0.39	
μ_A	-0.23		-0.28	
μ_B	-0.16		0.26	
μ_C	0.03		-0.07	
A (MHz)	3094.8	3093.50 (4)	2780.2	2780.97 (15)
B (MHz)	1189.9	1190.43 (26)	1257.2	1259.23 (26))
C (MHz)	903.3	903.33 (17)	990.8	990.44 (6)
D_J (kHz)	0.79	-49.57 (25)	2.50	–
D_{JK} (kHz)	-3.11	122.8 (10)	-9.31	–
D_K (kHz)	12.19	-72.0 (7)	20.35	–
d_1 (kHz)	0.18	33.91 (11)	0.20	–
d_2 (kHz)	1.14	-57.4 (3)	-1.03	–
Error (kHz)		44		79
N		9		5

3.4 Conclusions

This work has shown that tetramers of pure ethanol and mixed ethanol and water are formed in an array of low-energy conformers, with structural variation arising from the accessible gauche conformation states of ethanol sub-units. In the process

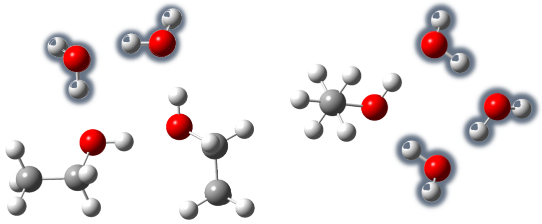

Figure 3.4: Comparison of isotopically labeled clusters and actual hydrogen bond position for the wttw conformer of $(D_2O)_2(CH_3CH_2OH)_2$ and the gwww conformer of $(D_2O)_3(CH_3CH_2OH)$.

of identifying tetramer structures with microwave signals, many potential minima were identified on the potential energy surfaces of these structures, demonstrating the myriad potential bonding patterns for these tetramers.

In particular, we see in this work that tetramer conformers that would otherwise be completely symmetric, i.e., one with all trans ethanol sub-units, are made polar by mixing ethanol and water in tetramer formation. These mixed clusters then both provide insight into mixing behavior of ethanol and water as well as rendering symmetric tetramer conformers polar, thus accessible experimentally.

It was interesting to note that although many different structures were computed as local energy minima for both the pure ethanol tetramers and mixed ethanol–water tetramers, only a few had sufficient dipole moments to be accessible experimentally. This highlights the importance of comparing experimental and computational studies of hydrogen bonding in small molecule clusters, as the full suite of low-energy conformations predicted by theoretical survey may not be observable. Experimental detection of at least a few of the conformational variations possible enriches our understanding of the intermolecular dynamics of alcohol and water mixing at the few molecule scale, as computational surveys allow us to examine potential minima that we are blind to using rotational spectroscopy.

Further, this work assists in building towards a robust description of intermolecular dynamics and mixing of water and ethanol. In particular, the $(H_2O)_2(CH_3CH_2OH)_2$ structures identified in experimental spectra indicate that some tetramer structures formed by water and ethanol already show signs of micro-aggregation, with two water molecules on one side of the ring of hydrogen bonding, and two ethanol molecules on the other side. This is by no means the only available bonding pattern, as it has been shown that all of the available cyclical conformers of the $(H_2O)_2(CH_3CH_2OH)_2$ tetramer are close in energy, but it still indicates that this type of separation on the molecular scale is feasible for water and ethanol mixing. This observation may then assist in modeling the complex details of water and ethanol micro-aggregation that influence the dynamics of the bulk system, furthering understanding of this mixing and refining predictive models.

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Chapter 4

SURVEY OF METHANOL AND WATER PENTAMERS

4.1 Introduction

As work in the Blake group progressed towards the study of larger clusters, the next species of interest was an exploration of the conformers of mixed alcohol and water pentamers. These species would represent another step towards understanding the bulk behavior of alcohol:water hydrogen bonding networks. Namely, of interest was whether or not microaggregation between alcohol and water would be observed in pentamers, as this cluster size allows for greater differentiation between the species.

In preparing to study pentamers and answer these questions, it was decided to change the alcohol of interest from ethanol to methanol. This decision was motivated by a number of factors; firstly, the higher vapor pressure of methanol would lead to higher content of methanol in the sample mixture, increasing the signal to noise and making detection of higher molecular weight species such as pentamers more achievable. Secondly, methanol is the smallest alcohol, so serves as a good starting point for future experimentation into the bulk properties of alcohol and water mixtures. By focusing on large methanol and water clusters, the Blake group research would be able to set a foundation for future work with larger alcohols.

Therefore, with methanol and water pentamers the target of interest, we began a survey of all possible planar conformers to explore the potential energy surface of these clusters. Planar conformations have been shown to be the most stable configuration in previous work (**Dutton2023**; Mejía, Espinal, and Mondragón, 2009), and by exploring all possible conformations, any trends in energy ordering between microaggregated and dispersed structures could be elucidated.

4.2 Methods

Computational

To begin the survey of the potential energy landscape of mixed methanol and water pentamers, density functional theory calculations were performed to identify local minima conformations. In the course of this work, a large number of conformers were identified at each relative abundance of methanol to water.

To keep track of the many conformers, a shorthand naming convention is used. Each structure has a ring of H-bonding with methyl groups lying above or below the plane of H-bonding. The ambiguous “above or below” the plane is distinguished by the right-hand screw rule with respect to the ring of H-bonds. To denote a methyl group is above the plane, an upward arrow (pictorially) or “u” (in text) is used; to denote a methyl group is below the plane, a “d” or downward arrow is used. A simplistic picture of the pure methanol pentamer, with its shorthand name and full structure, can be referenced in Figure 4.1. The naming convention for the pure methanol pentamer, from the top methanol following the H-bonds counterclockwise, yields uduud for methyl groups above, below, above, above, and below the plane of H-bonding, respectively. Water is always labeled “w", whether water’s free hydrogen is above or below the plane.

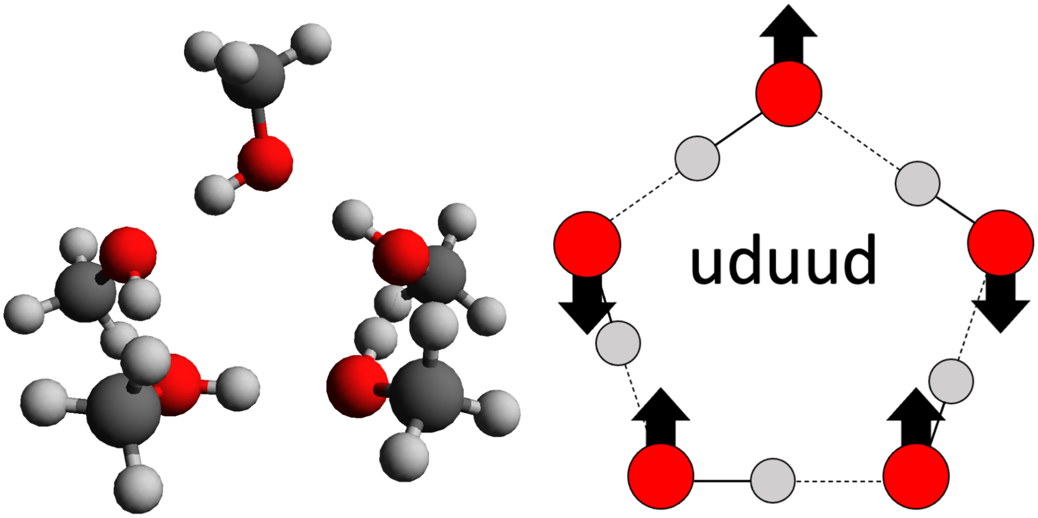

Figure 4.1: Full structure on the left, with the associated simple depiction and naming convention on the right.

The lowest energy methanol:water pentamers were retrieved from geometry optimizations using Gaussian 16 (Frisch et al., 2016), and subsequent frequency calculations with anharmonic corrections were performed on the optimized structures. Optimized geometries, rotational constants, quartic centrifugal distortion corrections, dipole moments, and free energies were calculated at the B3LYP level of theory using the 6-311++G(d,p) basis set. This level of theory and basis set combination has been shown to be sufficient in previous work (González, Mó, and Yáñez, 1998; Mandal et al., 2010), and the associated modest computational cost was desirable when performing calculations for the full array 65 unique pentamer clusters. Calculated rotational constants and anharmonic corrections were then used to simulate spectra with PGOPHER (Western, 2017), for comparison to experimental spectra.

For each additional methanol in the clusters, a new methyl rotor must be included in the analysis of splitting of the rotational states due to internal rotation. Barrier heights to methyl rotations were calculated with B3LYP/6-311++G(d,p) and these barrier heights were used to estimate the magnitude of splitting with XIAM (Hartwig and Dreizler, 1996). To keep the fitting consistent for each cluster with different numbers of internal rotors and therefore accuracy of XIAM prediction, only the A-states of all pentamer conformers were fit to experimental spectra, using a rigid-rotor Hamiltonian.

Experimental

The CPFTMW spectrometer was described in full previously (Dutton and Blake, 2022), so only a brief overview of the experiment is provided here.

Efficient formation of pentamers required a backing pressure of 3 atm Argon carrier gas bubbling through methanol first, then through water in a separate flask–that is, the sample flasks were connected. The water was heated to 60 °C, the point at which its vapor pressure is roughly equivalent to that of methanol at room temperature. When forming pure methanol clusters, water was taken off line and methanol was heated to 60 °C. Flow into the chamber was regulated to 50 sccm through a mass flow controller and the pressure of the chamber stayed below roughly 3 x 10^{-4} torr while sample underwent a continuous supersonic expansion through a 5.7 cm x 25

μm slit nozzle.

The chirp used in this experiment is 1.2 μs long and spans DC to 2 GHz (effectively 190 to 1820 MHz). The chirp is heterodyned with a local oscillator (LO) allowing for frequencies up to 18 GHz to be studied. The measurement is dual side-band, so one LO setting covers approximately 4 GHz. At each LO setting, 200 million 18 μs free induction decay acquisitions were averaged. Non-deuterated, perdeuterated methanol, and D_2O spectra were all fit with lines between 10 and 18 GHz, the region in which the population of rotational states is highest for the clusters of interest at the estimated rotational temperature of 10 to 20 Kelvin. The non-deuterated and perdeuterated methanol spectra are an average of 10 LO settings, or 2 billion acquisitions, while the D_2O spectrum is an average of 6 LO settings, or 1.2 billion acquisitions.

4.3 Results and Discussion

The 22 normal isotopologue pentamer conformers for which rotational constants, anharmonic corrections, dipole moment, and energies have been calculated are depicted in Figure 4.2. Of this full array of available conformers, rotational states associated with all 22 of the 22 pentamer conformers were observed in the experimental spectra, and fitted to derive rotational constants. Fitting was performed with the program SPFIT (Pickett et al., 1998), using the A reduction of Watson's Hamiltonian in the I^r representation.

Table 4.1 represents the singular minimum for the pure methanol pentamer, both

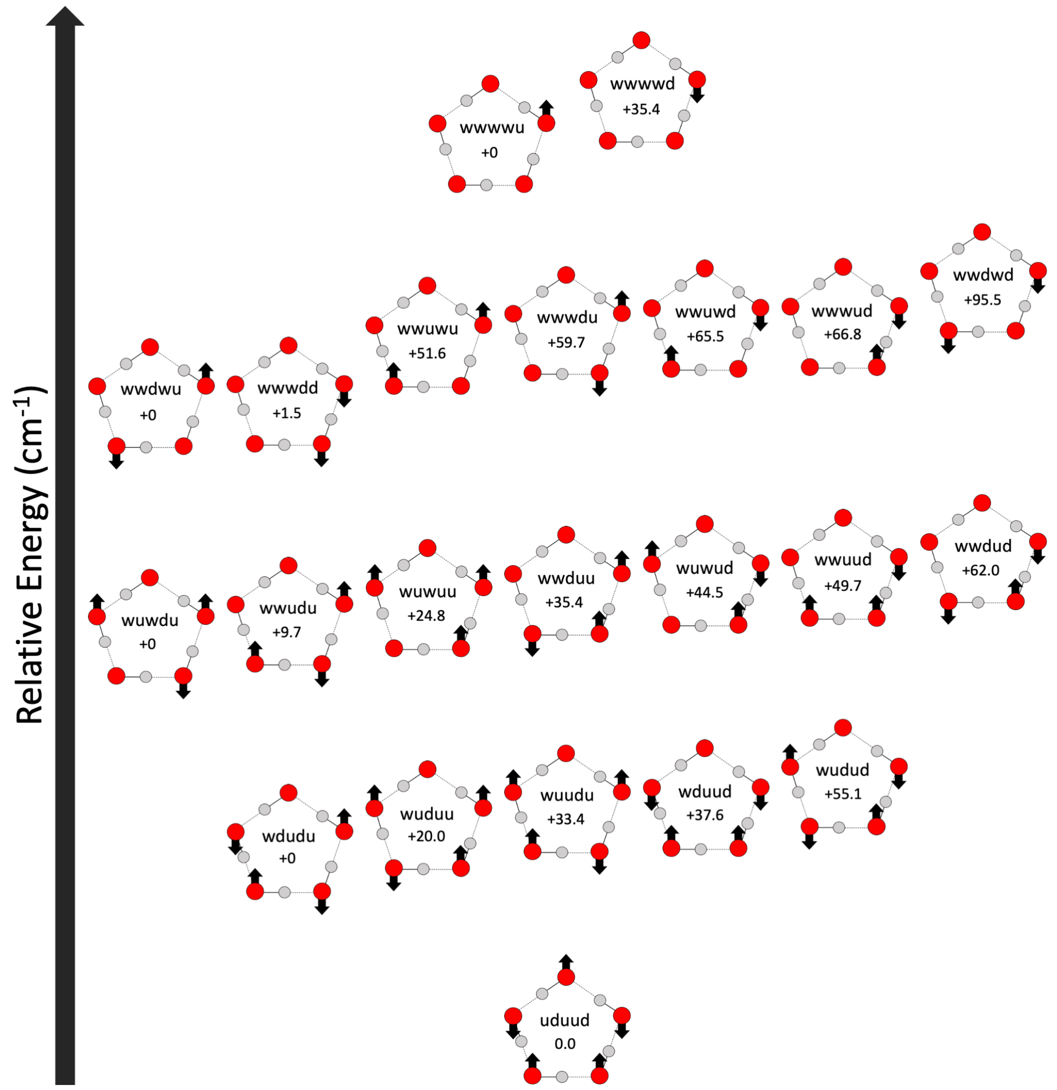

Figure 4.2: All non-deuterated pentamer conformers ordered by relative energies within each hydration level. Energy jumps between each hydration level are on the order 6500 cm^{-1}, or between 15 and 20 kcal/mol.

normal and d_4 isotopologues. Its inverse conformer, duddu, has the same calculated rotational constants thus we believe it is the same structure. Other permutations of u and d methyl groups either default to uduud/duddu by cycling starting points or place more than two adjacent methyl groups on the same side of the H-bonding plane. This crowding of the methyl groups on the same side of the plane results in much higher energy, and these structures are therefore not included in our analysis of minimum structures on the potential energy surface for the pure methanol pentamer.

Table 4.1: Calculated and experimental rotational constants for the pure methanol pentamer, both normal and D4 isotopologues. Parameters are fitted *via* SPFIT, using Watson's S-reduction of the Hamiltonian. N is the number of lines from the experimental spectrum fit, and the values in parentheses are the 1σ errors reported by SPFIT.

Ab Initio	uduud	D4-uduud
A /MHz	675.40	568.09
B /MHz	665.31	558.81
C /MHz	400.56	342.08
Δ_J /kHz	0.21	0.15
Δ_K /kHz	-0.24	-0.22
Δ_{JK} /kHz	0.16	0.18
δ_J /kHz	0.0023	0.0014
δ_K /kHz	10.4	7.73
Dipole /D	0.708	0.708
Fitted	uduud	D4-uduud
A /MHz	675.45 (18)	568.07 (13)
B /MHz	665.27 (11)	558.80 (8)
C /MHz	400.72 (32)	342.06 (8)
Δ_J /kHz	0.19 (4)	–
Δ_K /kHz	2.22 (27)	–
Δ_{JK} /kHz	-2.62 (3)	–
δ_J /kHz	0.04 (21)	–
δ_K /kHz	23.57 (28)	–
N	15	19
rms /kHz	88	36

With the addition of one water, we found five minima within 55 cm^{-1} of each other, as seen in Table 4.2. Similarly to the pure methanol pentamer, any permutation outside of these five either completely flips the cluster and returns to the same geometry or results in an energetically unfavorable crowding of methyl groups.

Table 4.2: Calculated and experimental rotational constants for all conformers of $(H_2O)(CH_3OH)_4$. Fit with Watson's A-reduction.

Ab Initio	wuduu	wduud	wudud	wdudu	wuudu
A /MHz	918.03	893.41	914.64	908.02	909.45
B /MHz	688.97	730.98	681.33	684.62	700.59
C /MHz	458.72	443.45	466.58	471.36	455.09
Δ_J /kHz	0.38	0.39	0.26	0.25	0.62
Δ_K /kHz	0.30	0.35	0.09	0.04	0.86
Δ_{JK} /kHz	-0.48	-0.61	-0.06	-0.02	-1.22
δ_J /kHz	0.02	0.01	0.03	0.03	0.02
δ_K /kHz	0.16	-0.03	0.39	0.44	-0.02
Dipole /D	0.549	0.832	0.911	0.876	0.593
Rel. Energy /cm^{-1}	20.0	37.6	55.1	0.0	33.4
Fitted	wuduu	wduud	wudud	wdudu	wuudu
A /MHz	917.92 (28)	893.63 (7)	914.64 (21)	908.02 (5)	909.48 (12)
B /MHz	688.99 (9)	731.03 (8)	681.30 (7)	684.62 (26)	700.39 (8)
C /MHz	458.83 (7)	443.42 (7)	466.43 (17)	471.39 (3)	455.00 (16)
Δ_J /kHz	0.38 (17)	0.43 (30)	-0.41 (7)	-0.32 (3)	-0.18 (7)
Δ_K /kHz	-0.30 (5)	-0.20 (13)	0.91 (13)	0.79 (6)	-1.45 (4)
Δ_{JK} /kHz	0.28 (6)	-0.071 (15)	-0.49 (20)	0.15 (10)	0.91 (4)
δ_J /kHz	0.089 (10)	0.0078 (10)	0.28 (37)	0.37 (21)	0.019 (10)
δ_K /kHz	-0.39 (6)	-2.57 (24)	0.44 (14)	0.54 (6)	-1.43 (5)
N	15	21	13	11	14
rms /kHz	60	63	76	84	87

Two and three water clusters, fits for which are shown in Tables 4.3 and 4.4, respectively, have seven minima each. One conformer of the three water cluster, wwwud, did not have enough observed lines for a fit of all quartic distortion constants. The lack of observable transitions for this conformer may be linked to lower abundance, which in turn could be due to the fact that as more conformers per hydration level became energetically available, intensity is spread between them. Further, it was shown computationally that pentamers with higher water content are commensurately higher in energy thus helping to explain the difficulty in observing these high water content clusters. Finally, the difficulty in fitting higher water content pentamers may be explained by the low vapor pressure of water relative to methanol, which leads to methanol favored clusters under expansion conditions.

To round out the survey of the mixed methanol and water pentamer potential energy space, both conformers of pentamers with four water and one methanol were observed. The results of fitting the rotational states for these species are shown in Table 4.5. It should be noted that the pure water pentamer is not observed due to its rotationally averaged symmetry (that is, lack of a permanent dipole moment), caused by the facile rotation of the OH bonds in this species, as in the pure water trimer.

As previously mentioned, the rotation of methyl rotors causes splitting into A and E state rotational transitions. The magnitude of splitting, estimated by XIAM (Hartwig and Dreizler, 1996), is on the order of 100 MHz. The lines are far enough apart to

Table 4.3: Calculated and experimental rotational constants for all conformers of $(H_2O)_2(CH_3OH)_3$. Fit with Watson's A-reduction.

Ab Initio	wuwdu	wuwuu	wwdud	wwuud	wuwud	wwduu	wwudu
A /MHz	1214.99	1201.82	1079.70	1151.98	1225.14	1160.33	1100.16
B /MHz	764.84	781.49	856.75	846.10	754.10	829.54	841.60
C /MHz	521.85	519.50	573.95	526.79	517.08	533.59	560.86
Δ_J /kHz	0.54	0.67	0.72	0.84	0.54	0.73	0.85
Δ_K /kHz	0.14	-1.55	1.49	1.45	-0.19	1.41	2.18
Δ_{JK} /kHz	-0.48	1.06	-1.85	-2.12	-0.091	-1.85	-2.54
δ_J /kHz	0.060	0.11	0.08	0.044	0.075	0.10	0.15
δ_K /kHz	0.22	2.17	-1.21	-0.85	0.46	-0.71	-1.75
Dipole /D	0.756	0.498	1.06	0.768	0.752	0.694	0.781
Rel. Energy /cm^{-1}	0.0	24.8	62.0	49.7	44.5	35.4	9.7
Fitted	wuwdu	wuwuu	wwdud	wwuud	wuwud	wwduu	wwudu
A /MHz	1214.94 (12)	1201.61 (22)	1079.44 (21)	1151.89 (22)	1225.30 (11)	1159.81 (7)	1099.58 (6)
B /MHz	764.89 (14)	781.57 (13)	856.77 (12)	844.55 (11)	754.18 (8)	829.55 (19)	841.75 (3)
C /MHz	521.58 (28)	519.52 (13)	573.12 (32)	526.62 (13)	516.97 (10)	532.91 (24)	562.91 (15)
Δ_J /kHz	0.28 (8)	0.46 (18)	0.36 (11)	-0.30 (19)	1.31 (3)	-2.41 (5)	-9.39 (7)
Δ_K /kHz	-2.04 (4)	-0.70 (4)	3.31 (4)	0.92 (30)	2.59 (9)	-1.66 (10)	-17.10 (16)
Δ_{JK} /kHz	-0.32 (12)	0.39 (6)	-5.56 (4)	-1.22 (5)	-3.88 (12)	1.11 (15)	41.56 (28)
δ_J /kHz	0.0079 (25)	0.83 (12)	0.32 (26)	0.14 (12)	0.031 (21)	1.57 (4)	2.42 (4)
δ_K /kHz	0.30 (4)	-2.33 (3)	-3.37 (4)	-0.83 (4)	0.019 (4)	-1.52 (12)	0.034 (26)
N	12	13	11	17	16	20	9
rms /kHz	43	53	56	76	81	92	208

Table 4.4: Calculated and experimental rotational constants for all conformers of $(H_2O)_3(CH_3OH)_2$. Fit with Watson's S-reduction.

Ab Initio	wwuwu	wwdwd	wwuwd	wwwdd	wwdwu	wwwdu	wwwud
A /MHz	1663.68	1630.05	1737.44	1289.13	1729.16	1255.41	1242.80
B /MHz	878.98	895.64	866.89	1149.00	862.09	1153.53	1159.73
C /MHz	618.87	631.68	613.30	639.98	609.56	660.30	673.01
Δ_J /kHz	0.68	0.79	0.56	1.48	0.51	0.93	0.90
Δ_K /kHz	4.76	4.65	2.32	1.30	3.20	1.17	0.94
Δ_{JK} /kHz	-2.44	-2.71	-1.21	-2.59	-1.36	-1.60	-1.51
δ_J /kHz	-0.10	-0.13	-0.071	-0.067	-0.076	-0.044	-0.0086
δ_K /kHz	0.075	0.071	0.12	0.33	0.088	0.095	0.12
Dipole /D	0.689	0.671	0.921	0.669	0.880	0.916	0.936
Rel. Energy /cm^{-1}	51.6	95.5	65.5	1.50	0.0	59.7	66.8
Fitted	wwuwu	wwdwd	wwuwd	wwwdd	wwdwu	wwwdu	wwwud
A /MHz	1663.87 (14)	1630.12 (14)	1737.49 (15)	1289.22 (4)	1729.21 (15)	1255.54 (8)	1243.06 (21)
B /MHz	879.09 (7)	895.69 (18)	866.91 (6)	1148.91 (15)	862.16 (12)	1153.57 (4)	1159.42 (15)
C /MHz	618.61 (11)	631.73 (19)	613.25 (7)	640.05 (18)	609.08 (14)	660.81 (29)	673.00 (5)
Δ_J /kHz	1.77 (7)	1.42 (9)	0.81 (6)	3.11 (29)	0.57 (6)	2.05 (11)	–
Δ_K /kHz	6.19 (18)	3.22 (17)	1.71 (15)	7.02 (8)	2.54 (10)	-1.32 (19)	–
Δ_{JK} /kHz	-5.77 (25)	-2.06 (26)	-1.00 (17)	-9.51 (10)	-0.83 (16)	1.66 (30)	–
δ_J /kHz	-0.45 (4)	-0.26 (3)	-0.27 (25)	-0.98 (14)	-0.18 (25)	-0.46 (5)	–
δ_K /kHz	1.06 (12)	0.67 (12)	0.49 (6)	16.8 (24)	0.40 (5)	11.2 (31)	–
N	12	14	17	13	17	12	4
rms /kHz	58	61	64	66	93	100	146

Table 4.5: Calculated and experimental rotational constants for all conformers of $(H_2O)_4(CH_3OH)$. Fit with Watson's A-reduction.

Ab Initio	wwwwu	wwwwd
A /MHz	1976.91	1946.88
B /MHz	1215.52	1235.53
C /MHz	775.60	790.47
Δ_J /kHz	2.06	2.44
Δ_K /kHz	3.57	4.82
Δ_{JK} /kHz	-5.37	-6.83
δ_J /kHz	0.49	0.51
δ_K /kHz	-2.38	-3.47
Dipole /D	0.840	0.836
Rel. Energy /cm^{-1}	0.0	35.4
Fitted	**wwwwu**	**wwwwd**
A /MHz	1976.71 (24)	1946.66 (20)
B /MHz	1215.70 (3)	1235.56 (9)
C /MHz	775.45 (13)	790.67 (14)
Δ_J /kHz	0.91 (13)	-0.70 (12)
Δ_K /kHz	-2.29 (5)	-5.75 (4)
Δ_{JK} /kHz	1.10 (6)	8.22 (5)
δ_J /kHz	0.37 (14)	0.83 (6)
δ_K /kHz	-3.05 (5)	-6.66 (8)
N	12	9
rms /kHz	56	95

be resolved, and have been observed in experimental spectra. For consistency, only A-A type transitions were fully fit however, given that in clusters with four or five methanol monomers, there are more rotors than XIAM can precisely predict. To approximate the magnitude of splitting in clusters with three or more methyl groups, some groups were approximated as having the same local environment and therefore treated as one such methyl rotor, thereby reducing to two 'types' of rotors. Since this approximation was made, we cannot confidently predict the location of non-A-A transitions, thus we fit only those A-A transitions to determine cluster geometry. However, we know from this approximated XIAM fit that the split transitions are far enough apart from A-A lines as to not affect the accuracy of our line assignment, nor increase the error in line position, as was observed in studies on ethanol and water clusters.

In the present work, the agreement between predicted rotational constants and experimentally derived rotational constants is extremely good, with error in the primary rotational constants typically less than a megahertz. This may be explained by the strong donor-acceptor hydrogen bonding in the clusters, in that this stability leads to well-defined minima on the potential energy surface. These well-defined minima are thus in turn better described by the DFT methods used herein. In addition, some switching between the asymmetric and symmetric reduction of the Hamiltonian is observed in the internal workings of the program used to fit the experimental spectra, SPFIT (Pickett, 1991). This variation leads to sign errors in the quartic distortion constants for these preliminary fits, and will be resolved in ongoing work.

Figure 4.3 displays a section of the 8 GHz experimental spectrum with non-deuterated methanol and water. This section of the spectrum has a sample of each hydration level besides pure methanol (which was assigned separately). After fitting a spectrum, dual resonance experiments were performed to confirm the assignments of the lines listed. Isotopic substitution will be used as a secondary means to confirm the correct conformer assignment.

To further verify geometries and improve confidence in conformer assignments, 22 d_4-methanol:water, 21 methanol:D_2O clusters, and 22 singly deuterated structures

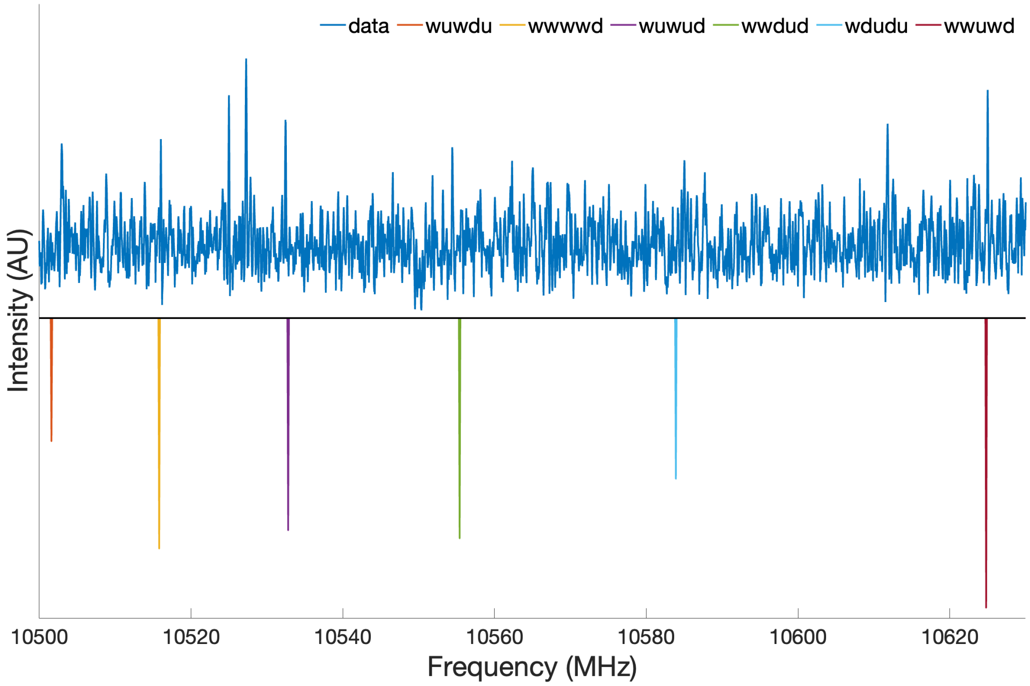

Figure 4.3: 150 MHz sample of our 8 GHz non-deuterated spectrum which encompasses lines for a 1, 2, 3, and 4 water species of the mixed pentamers.

were studied with the same expansion conditions and fitting routines previously described. Fitting these species is ongoing, with 40 of the 43 D_2O and D_4 clusters preliminarily fit with experimental lines, and all 22 of the singly deuterated structures. This brings the total number of pentamer conformers presented with *ab initio* calculations to 87, with 84 of those fit to experiment so far. Finalized deuterated fits will serve to confirm correct conformer assignment and the singly deuterated species will allow for geometric analysis *via* the Kraitchman equations.

Within each group of clusters (0, 1, 2, 3, or 4 waters) the conformers are close in energy, with the largest difference being less than 100 cm^{-1}. However, large energy gaps were calculated in the free energies from one group of clusters to another, on the order of 15 to 20 kcal/mol, or 6500 cm^{-1}. This may be explained by the electron donating characteristics of the methyl group strengthening the ring of hydrogen bonding with higher methanol content. Net cooperativity for all clusters remains two for each conformer studied here since the cyclic hydrogen bonding scheme is unchanged, but as methanol is replaced with water, the bonds lengthen and the energy rises. The R_{O-O} distance for the pure water pentamer is 2.76 Å (Liu et al., 1997). We find a steady decrease in bond length with additional methanol leading to pure methanol pentamer R_{O-O} distances averaging 2.71 Å. These bond distances will be confirmed with Kraitchman analysis; preliminary data shows little change in the position of a hydrogen involved in hydrogen bonding between the *ab initio* predicted position and the Kraitchman calculated position. This implies the suitability of predicted structures for geometric analysis, and thus supports the observed trend of decreasing O-O distance with additional methanol content.

The abundance of each cluster across hydration levels depends on experimental conditions, but those of the conformers within each hydration level can be used to show formation preferences. To estimate relative abundances, we averaged the signal-to-noise of each peak that was used for fitting and divided by the total dipole moment. There did not appear to be a significant abundance difference for each conformer within any of the hydration levels.

Two and three water clusters are where observations about a preference for homogeneous methanol and water mixing vs micro-aggregation could be made. All seven of the conformers at both hydration levels had relative abundances equal within error. However, the average root means squared (rms) error of rotational constant fits for conformers with dispersed methanol and water is more than twice that of the conformers with micro-aggregation when including all isotopologues fit. Taken together, these results imply no great preference in cluster formation between microaggregated structures and interspersed structures, though perhaps an increased difficulty in fitting structures with even mixing of methanol and water. This increased fitting error could be due to a number of things–one explanation may be that the high probability of exchange of hydrogen and deuterium raises the error in isotopologue fits. Another explanation may lie in the large amplitude motion of these clusters. As internal rotation can split the rotational states, so too can the rotational spectrum be shifted due to the large amplitude motion (LAM) of the underlying cluster geometry. Perhaps, in interspersed water and methanol clusters, this LAM is more prevalent, or more impactful. Future high resolution studies would be beneficial in testing out this effect and conclusively determining the cause of the increased fitting error observed for interspersed clusters. In addition, these future high resolution studies could use the fully fit A-E splitting to large amplitude effects in different cluster conformers, determining whether any potential difference between aggregated and evenly dispersed clusters exists.

4.4 Conclusions

The aim of this rotational spectroscopy study was to survey the potential energy landscape of neat and mixed methanol and water pentamer conformers. From this work, the rotational constants for 22 conformers have been fit from experimental data. No clear distinction between microaggregated and interspersed conformers was observed, supporting the idea that methanol and water mix freely in small cluster formation.

In all of these clusters, a planar hydrogen bonding motif is observed, leading to a net cooperativity of two. Higher cooperativity clusters, i.e., clusters with a more 'three-dimensional' structure were proposed, but were not found to be minima on the potential energy landscape for methanol and water pentamers. This result indicates that for pentamers, a planar, ring-like structure is still the lowest energy, as has been the case for tetramers and trimers of mixed alcohol and water in previous work (Dutton and Blake, 2022; Mejía, Espinal, and Mondragón, 2009; Pérez et al., 2012).

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Chapter 5

COOPERATIVITY IN METHANOL AND WATER PENTAMERS AND HEXAMERS

5.1 Introduction

In the wake of the COVID-19 global pandemic, a universal appreciation for hand sanitizer has grown (Abuga and Nyamweya, 2021). There is little doubt as to the efficacy of this substance in sterilizing against viruses and bacteria, a property arising from the antiseptic properties of alcohol. Alcohol and water mixtures are used beyond hand sanitizer, ubiquitous in chemical synthesis as solvents or in popular libations. Despite this near universal use of applicability, the fundamental properties of the hydrogen bond network that defines the mixing of alcohol and water are still ill-defined (Nyamweya and Abuga, 2021; Soper et al., 2005; Lenton et al., 2018). Further, beyond our global pandemic woes, and even our solar system, alcohol and water mixtures are also of relevance to the study of interstellar ice, where methanol, water, carbon monoxide and carbon dioxide are posited to be the critical components of ice on interstellar grains (He and Vidali, 2017; Müller, 2022; Goto et al., 2021; Dawes, Mason, and Fraser, 2016).

Many researchers look to further their understanding of the dynamics and energetics of alcohol:water mixing through the computational modeling of these hydrogen bond networks (Bosma, Fried, and Mukamel, 1993). This is accomplished through molecular dynamics simulations (MD), which rely on accurate force fields to simulate the bulk behavior of the system. Herein lies one difficulty in this modeling; generating accurate force fields to mimic the complex behavior of hydrogen bonding between alcohol and water is a complex task. A common strategy in recent years has been to build these force fields from the ground up–to start with experimentally determined energy ordering of alcohol and water monomers, dimers, trimers, etc. Using this empiric data for small clusters, the algorithm for the force field will then extrapolate over larger and larger clusters until it simulates the behavior of the bulk system (Bull-Vulpe et al., 2021; Riera et al., 2020).

Therefore, in order to further the development of more accurate force fields, exact geometric analysis and energetic ordering of small molecule clusters is crucial. Once more, an ideal tool for the study of the geometry of these small alcohol:water clusters is chirped pulse Fourier-transform microwave spectroscopy (Brown et al., 2008; Finneran et al., 2013). This tool allows for precise structural detail to be gleaned from the empiric determination of rotational constants via the observation and subsequent fitting of observed rotational modes in the GHz-spanning spectrum obtained.

One particular structural question that CPFTMW can assist in answering is the question of the site-specific and net cooperativity in small molecule clusters (Mejía, Espinal, and Mondragón, 2009; Masella and Flament, 1998; Pérez, Zaleski, et al., 2014). Water in particular has been observed to have varying cooperativity in different conformers of high-order molecular clusters (Pérez, Muckle, et al., 2012; Pérez, Zaleski, et al., 2014). This property arises from the availability of multiple hydrogen bond donor and acceptor sites on the water molecule, which greatly expands the available conformations of a certain cluster size. As such, the larger a water cluster grows, the more available structural conformers exist, increasing the complexity of the potential energy surface and informing the need for further studies, both experimental and computational. With the knowledge of the existing complexity of the water cluster cluster formation, a natural question arises when considering mixtures of water and alcohol; does this similar variation in net cooperativity exist? Further, at what cluster size does the three dimensionality exhibited in water clustering arise in mixed alcohol water clusters? Finally, is homogeneous mixing between methanol and water observed in these higher dimensionality clusters, or is there any microaggregation between the species?

To this end, this work aimed to study the structure of mixed methanol and water pentamers and hexamers. CPFTMW was used to collect rotational spectra from 10 to 18 GHz of mixed methanol and water clusters with varying ratios of methanol and water. These data sets allowed for the fitting of rotational constants for the lowest energy conformers of each type of hexamer or pentamer, and the structural parameters extracted from this rotational analysis were used to investigate the changes in geometry upon water mixing with methanol, as well as the trends in cooperativity for each conformer of each type of cluster observed.

5.2 Experimental

A full array of available neat and mixed water and methanol pentamers were analyzed computationally and experimentally, the full experimental details for which are presented in Chapter 4. The results of this survey of the pentamer potential energy space were used to inform the experimentation with hexamers.

To begin the hexamer analysis, conformers of pure water hexamers, pure methanol hexamers, and mixed methanol and water hexamers were optimized using density functional theory calculations through the Gaussian program (Frisch et al., n.d.). The B3LYP level of theory and 6-311g++(d,p) basis set were used, as these were shown to provide sufficient accuracy for comparison to rotational spectroscopy experiments in our previous work with smaller alcohol:water clusters. Frequency calculations were performed with anharmonic corrections to yield quartic distortion constants.

Experimental data were collected via the high-throughput CPFTMW apparatus described in previous chapters. Methanol, water, or both were prepared at a backing pressure of 3 atm, and expanded continuously through a 5.7 cm by 25 micron slit nozzle. Backing pressure in the vacuum chamber stayed below $4 * 10^{-4}$ torr. Prior to expansion, water was heated to approximately 60 °C so as to increase the fraction of water in the gas phase. These expansion conditions led to a rotational temperature estimated to be between 10 and 20 K, as determined by comparison of observed line relative intensity to spectra simulated with the rotational spectra software PGOPHER (Western, 2017). Isotopic substitution experiments were performed by expanding D_2O with methanol or perdeuterated methanol with H_2O. Singly deuterated clusters were then formed through isotopic exchange, and fits were confirmed and O-O distance was analyzed *via* rotational constant fits for these singly deuterated structures.

Predicted lines were observed in rotational data for pure methanol and mixed water and methanol hexamers, and iteratively fit with the program SPFIT (Pickett, 1991). The splitting of rotational states from internal rotation of the methyl rotor was predicted was predicted with the program XIAM (Hartwig and Dreizler, 1996), however, for accuracy, only A-A states were fit with a rigid-rotor Hamiltonian, due to the presence of many internal rotors. The magnitude of the predicted splitting from XIAM was on the order of 100's of MHz, meaning that split lines would be far enough away to fit only the A-A states, once the appropriate internal rotation symmetry patterns were observed.

For the pure methanol hexamer, the lowest energy conformer computationally found is a completely symmetric structure with hydrogen bonding in a planar, ring-like pattern. This conformer is thus undetectable via MW spectroscopy due to the lack of a permanent dipole moment. By altering the pattern of methyl group orientation around the ring of hydrogen bonding however, a non-symmetric conformer is formed at similar energy. This conformer has a net dipole moment of 0.27 debyes; weak enough to be right on the edge of detectability with our current instrumentation, as our previous work with tetramers and hexamers has detected species with similar dipole moments (**Dutton2023**; Dutton and Blake, 2022). In addition, this conformer is within 1 kcal/mol, or 350 cm^{-1} of the symmetric hexamer conformer, meaning that it is similar enough in energy that formation during sample expansion is probable.

In contrast, pure water hexamers have been shown in previous studies to follow higher cooperativity bonding patterns, that is conformers with more '3-dimensional' geometry (Pérez, Muckle, et al., 2012). Namely, water hexamers have been shown to form three main conformers, coined the prism, book, and cage conformers. In this work, the cage conformer is shown to be the lowest in energy, followed by the prism, with only the cage conformer previously identified in expansions with argon as a carrier gas, and all conformers seen in expansions with Ne or He as a carrier gas. These two conformers are also the highest cooperativity structures, with net cooperativity of three for the prism conformer (all sites have cooperativity=3), and net cooperativity of 2.66 (that is, four sites with cooperativity=3, and two with cooperativity=2), for the cage conformer.

Thus, mixed water and methanol hexamers were explored using the framework of the geometry of the available pure water conformers, specifically, the cage and prism conformations. These were identified as the most likely to be observed in alcohol:water mixed hexamers, due to the presence of lower cooperativity sites in these conformers. The free hydrogens present in the pure water structures were seen as ideal places to 'slot in' a methyl group in the mixed methanol:water analog structure. The book conformer of the pure water hexamer was also considered, however, this structure was of less interest given how close this structure is to the planar structures of mixed water and methanol pentamers and hexamers (which we have assigned, as seen in Chapter 4), and because it was known to be a higher energy conformer for the pure water hexamer. Neither the prism or the book conformers were observed in expansion of pure water with argon in previous work (Pérez, Muckle, et al., 2012), thus the proposed mixed methanol and water prism structure was used a measure to investigate whether these '3-dimensional' clusters are closer in energy in the methanol and water mixed hexamers than for the pure water clusters. Finally, while hydrogen-bond tunneling between equivalent prism conformers (Pérez, Muckle, et al., 2012) of the pure water hexamer has been observed, this behavior was not possible in the substituted structures due to the presence of fewer free hydrogens, having replaced many of them with methyl groups.

With this approach, three mixed methanol and water hexamer conformers were observed in experimental data. One mimics the prism conformer of the pure water hexamer, and is a 50:50 mix of methanol and water, as shown in Figure 5.1, along with the pure water prism conformer for comparison. The other two both follow the cage conformer of the pure water hexamer, and are quite similar in structure, differing only in the number of methanol molecules; one has three, and the other four. These conformers are shown in Figure 5.2, also with the pure water cage conformer for comparison. In all observed conformers, the methanol molecules are placed where free hydrogens were in the pure water analog structures, allowing for a direct

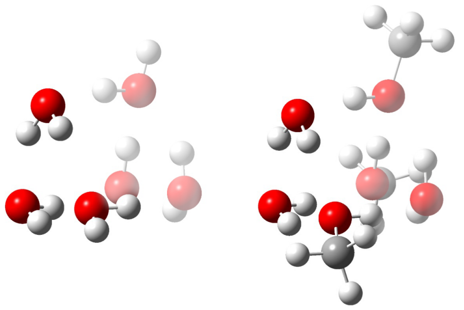

Figure 5.1: Prism conformer of the pure water hexamer (left), and mixed methanol and water cage conformer with three methanol molecules (right). All structures optimized at the B3LYP level of theory with 6-311g++(d,p) basis set using Gaussian 09 (Frisch et al., n.d.).

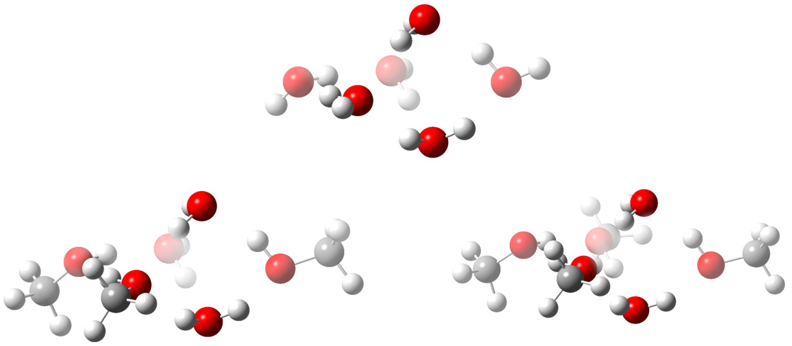

Figure 5.2: Cage conformer of the pure water hexamer (top), and mixed methanol and water cage conformers with three methanol (left) and four methanol (right) molecules. All structures optimized at the B3LYP level of theory with 6-311g++(d,p) basis set using Gaussian 09 (Frisch et al., n.d.).

comparison of the energetics and geometry of the pure water and mixed methanol and water hexamers without changing the net cooperativity of the structures.

5.3 Results

From the work with neat methanol and mixed methanol and water pentamers described in the previous chapter, 22 unique conformers were identified as potential minima, 21 of which were observed in experimental data. All of these conformers, regardless of the relative amounts of water and methanol, were ‘planar’ in geometry, with net cooperativity of two. In addition, no preference for formation of inhomogenous clusters was observed; that is, no inclination towards microaggregation between methanol and water was shown. For full details, see Chapter 4.

From the fitting of observed rotational lines for methanol and water hexamers, three different conformers of mixed hexamers and one of pure methanol hexamer were observed. These four structures represent three unique geometries for hexamer structures, with varying cooperativity.

For the pure methanol hexamer, the structure is again best described as ‘planar’; all the hydrogen bonds are in the same plane, forming a ring. For each methanol monomer in this hexamer conformer, the cooperativity is two, leading to an overall net cooperativity of 2 as well. This follows the trend of small methanol clusters– recent work in this group has shown that methanol pentamers follow the same bonding motif. In exploring the variations on the planar conformations of the methanol hexamer, one conformer was shown to have a dipole moment greater than zero, and as such is reffered to as the asymmethric MeOH hexamer. This nonzero dipole moment allowed for empiric determination of rotation constants *via* fitting the rotational spectrum, the results of which are shown in Table 5.1.

Table 5.1: *Ab initio* predicted and experimentally derived rotational constants for the ‘asymmetric’ MeOH hexamer.

	Ab initio Asymm. MeOH Hex.	Fitted Asymm. MeOH Hex.
A/MHz	477.00	477.32 (5)
B/MHz	420.87	420.78 (27)
C/MHz	287.08	287.03 (7)
D_J/kHz	0.13	-0.12 (27)
D_{JK}/kHz	0.14	1.83 (10)
D_K/kHz	-0.14	-1.76 (12)
d_1/kHz	0.03	0.08 (7)
d_2/kHz	0.69	-5.4 (4)
μ_a/D	-0.2209	
μ_b/D	0.1463	
μ_c/D	0.0019	
N		10
rms/kHz		27

Notably, when more three-dimensional bonding motifs for pure methanol hexamers were explored, none were shown to be local minima on the potential energy surface for this species. This lack of available conformers with higher net cooperativity and/or more three dimensional bonding patterns shows a divergence from the behavior of neat water.

This behavior is explained by the fact that there are fewer sites for hydrogen bonding for methanol than for water; three for methanol, and four for water. In addition, there is steric hindrance from the methyl group to contend with, limiting the space around the lone pairs that could potentially act as hydrogen bond acceptors.

This behavior also follows the trend seen in smaller clusters. For example, the stationary points on the potential energy surface for the methanol and water trimer are all planar (González, Mó, and Yáñez, 1998), as are the conformers available for methanol and water tetramers (Mejía, Espinal, and Mondragón, 2009; Mandal et al., 2010). The energy difference between 'branched' structures and these planar, cyclic hydrogen bonding motifs is significant, at several kcal/mol. This pattern favoring these structures with net cooperativity of 2 shows the inherent stability of these ring-like conformers from this higher cooperativity. As clusters of mixed methanol and water grow larger however, the question arises whether even greater cooperativity is possible.

With this fundamental difference in neat methanol hexamer conformers from those of neat water, the question as to what is the tipping point between these bonding motifs. That is, at what relative percentages of water and methanol are water-like hexamer structures available? From these studies, it seems that the answer lies in examining the cooperativity of each water molecule involved in hexamer conformers. If a monomer within a hexamer structure is hydrogen bonded to its neighbors with two hydrogen bond donors, then this monomer position may not be substituted for a methanol. Whereas if a monomer subunit has a free hydrogen, not engaged with hydrogen bonding, a methanol monomer may be 'slotted in' at this position without drastically altering the conformer geometry. In the previously studied water conformers, there are three positions available for methanol in the prism structure that have cooperativity of 3, but a free hydrogen that allows room for the methyl group. Specifically, each of these sites could be labeled 'DAA', in that they are accepting two hydrogen bonds, and donating one.

In the cage conformer, there are 4 such positions in the structure, two with cooperativity of 3 (similarly DAA) and two with cooperativity of 2. We choose to analyze the structures with the maximal methanol 'slotted in,' as a proxy to analyze the most even mixture of methanol and water. In addition, the cage conformer with only 3 methanol 'slotted in' is chosen as a target as a direct comparison to the prism structure with the same mixing ratio.

Following this logic, three potential mixed water and methanol hexamers were proposed and calculated, and identified in experimental spectra. Each of these structures has the maximum amount of methanol while preserving the pure water conformer structure. In other words, in each of these structures, every water molecule with a free hydrogen has been converted to a methanol monomer. These three hexamer conformers are a prism conformer with 3 methanol monomers, named Prism 3M, a cage conformer with 3 methanol monomers, named Cage 3M, and a cage conformwer with 4 methanol monomers, called Cage 4M. Similar to the pure water hexamer conformers, these conformers are close in energy, with less than a kcal/mol difference. The cage conformer is again the lowest in energy, but the prism conformer was seen in experimental data, a marked difference from the pure water expansion. This may be attributed to energetic differences between the mixed and pure hexamer conformers, but also could be the result of the combination of a planar expansion and higher averaging afforded by the high throughput experimentation. The results of fitting the experimental rotational spectra for these species are shown in Table 5.2 and Table 5.3.

Table 5.2: *Ab initio* predicted and experimentally derived rotational constants for the prism conformer of the three water, three methanol hexamer.

	Ab initio Prism 3M	Fitted Prism 3M
A/MHz	1036.128	1032.83 (11)
B/MHz	639.391	641.79 (6)
C/MHz	548.933	548.83 (3)
D_J/kHz	0.081	-9.77 (17)
D_{JK}/kHz	0.309	-2.4 (3)
D_K/kHz	0.049	12.17 (18)
d_1/kHz	0.008	12.04 (16)
d_2/kHz	-0.028	3.47 (21)
μ_a/D	-1.9464	
μ_b/D	0.3877	
μ_c/D	-1.9384	
N		16
rms/kHz		71

Table 5.3: *Ab initio* predicted and experimentally derived rotational constants for the cage conformers of the three water, three methanol hexamer and the two water, four methanol hexamer.

	Ab initio Cage 3M	Fitted Cage 3M	*Ab initio* Cage 4M	Fitted Cage 4M
A/MHz	1339.14	1339.13 (5)	924.37	924.66 (3)
B/MHz	524.27	524.72 (4)	524.03	522.13 (26)
C/MHz	450.02	449.98 (5)	392.04	392.09 (9)
D_J/kHz	0.080	0.66 (30)	0.069	1.54 (25)
D_{JK}/kHz	.366	5.23 (4)	0.44	4.00 (13)
D_K/kHz	.185	-5.98 (4)	-0.28	-5.57 (12)
d_1/kHz	.011	0.56 (11)	0.017	3.08 (23)
d_2/kHz	.218	4.50 (4)	0.30	-8.84 (10)
μ_a/D	1.6411		-1.6263	
μ_b/D	-0.8584		-0.7572	
μ_c/D	-0.5672		0.4862	
N		14		20
rms/kHz		126		107

In these fit structures, we see that the these represent the maximal mixing ratio between methanol and water in hexamers that will still maintain 3D conformers. In other words these conformers represent the ‘tipping point’ between the planar conformers of all pentamer conformers and pure methanol hexamers and the 3D conformers of the pure water hexamers.

In addition, the results of the analysis of the mixed ‘3D’ structures show methanol easily slotting in at the maximum number of positions with cooperativity = 2, or cooperativity = 3 with only one donor interaction, in these hexamer structures. Previous work studying the shifts in vibrational modes associated with integrated vs. microaggregated methanol and water mixtures have shown that at a mixing ratio of about 60% methanol, the bonding behavior between methanol and water changes, perhaps implying inhomegeneity in mixing between methanol and water (Dawes, Mason, and Fraser, 2016). This implies an observed tipping point between molecularly mixed methanol and water in ice and microaggregated behavior in the bulk. The results presented herein agree with this tipping point, in that the maximum methanol content of these higher cooperativity hexamer structures is on average near 60% (50% for the prism structure, 67% for the cage structure).

From examining these structures, we see the geometry of the pure water conformer is well mimicked in the mixed prism and cage conformers, with minimal distortion upon inclusion of methanol. This is verified via the fitting of singly deuterated isotopologues to confirm hydrogen position of an atom involved in hydrogen bonding between water and methanol in each conformer. The resulting Kraitchman analysis shows good agreement between the calculated minimum geometry and the experimentally determined H position, which implies that the computationally derived structures may be used for analysis of the conformer.

These computed structures show the same net cooperativity as the pure water hexamer, as well as similar O-O bond distances. In the pure water cage conformer, O-O distance ranges from around 2.7 to 3.0 Angstroms (Pérez, Muckle, et al., 2012); in Cage 4M structure, the O-O distance between adjacent methanol monomers is between 2.7 and 2.8 Angstroms, while the O-O distance between methanol and water monomers is closer to 3.0 Angstroms. This may not be due simply to interactions between water and methanol, rather, the authors posit that slightly longer O-O distance is instead correlated with higher cooperativity, as the water monomers in the Cage 4M structure all have cooperativity of 3. This theory is supported by the trend in in O-O distance in the pure water cage conformer, for the longest O-O distances in that structure also involved monomers with cooperativity = 3. Specifically, it is observed that the longest O-O distances have sites with cooperativity of 3 acting as H-bond donors in both pure water and mixed hexamers.

Further support comes from the analysis of the O-O distances in the Cage 3M conformer. In this structure, we again see that the longest O-O distance, at 3.0 Angstroms, is between a water molecule with cooperativity of 3 acting as an H-bond donor to a water molecule with cooperativity of 2. Overall, O-O distances in the Cage 3M conformer again range from between 2.7 to 3.0 Angstroms, showing good agreement with the pure water cage structure once again.

For the prism conformer of the water hexamer, O-O distance is also between 2.7 and 3.0. In the mixed structure, the Prism 3M conformer, we see a range between 2.7 and 2.9 Angstroms. Once again, the longest O-O distances can be found where higher cooperativity sites act as H-bond donors.

In order to study the strength of the hydrogen bonding interactions between water and methanol, single methanol substitution into the pure water cage conformer was calculated at a cooperativity = 2 position and a cooperativity = 3 (DAA) position. These optimized geometries showed that the methanol placement in a cooperativity = 3 position was slightly more stable, by about 0.2 kcal/mol. This stability follows the previously observed trend in smaller clusters, in which the hydrogen bonding in methanol-methanol and methanol-water clusters was even stronger than that of pure water clusters. Overall, the observed stability in mixed methanol and water hexamers at high cooperativity sites underscores a greater pattern of increased stability in these mixed clusters, particularly as observed here where methanol acts as an H-bond acceptor. In addition, the trend in increased stability upon substitution of water for methanol supports the trend in decreased O-O distance observed for H-bond acceptor positions, all supporting a picture of highly stable mixed clusters of methanol and water.

5.4 Conclusions

In this work, neat methanol and neat water hexamers were compared to mixed conformers via experimental observation with CPFTMW. The observed mixed conformers show that mixed methanol and water hexamers represent the transition from planar cluster formation to three dimensional clusters mimicking the pure water conformers previously observed. Analysis of the cooperativity and resulting effect on O-O distance in these conformers shows good agreement between the pure water structures and the mixed methanol and water structures.

Overall, these results provide some quantitative support for the observed strong hydrogen bonding interactions between methanol and water. The facile inclusion of methanol into the hydrogen bonding network of pure water hexamers echoes the mixing dynamics of these substances in the bulk. Future work on large clusters of mixed methanol and water may help support this trend and provide more detailed explanation for the anomalous bulk properties of this mixture, namely the low entropy of mixing.

Further, the observation of three dimensional, and therefore higher net cooperativity conformers of mixed methanol and water hexamers begins to show potential patterns for the hydrogen bonding network in the bulk mixture. As shown, these higher cooperativity structures are easily formed, implying higher cooperativity in the local environment for methanol and water mixtures, and perhaps elucidating some of the available configurations during dynamic hydrogen bond network changes in these mixtures.

Finally, the observation of facile mixing between methanol and water in both the planar and higher cooperativity structures has shown no preference for microaggregation between methanol and water in hexamers. However, the mixing ratios represented in the higher cooperativity structures may represent the maximal amount of methanol incorporated into these structures, supporting the previous evidence in ice studies that inhomegeneity may be observed at mixing ratios above 60%. While these previous studies are on solid state methanol and ice mixtures, future work on higher order clusters may help elucidate this trend in the gas phase.

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Chapter 6

CONCLUSION

6.1 Summary

To begin the work presented in this thesis, a novel high-throughput instrument for chirped pulse Fourier-transform microwave spectroscopy was developed. The sensitivity of this instrument under pulsed jet conditions was benchmarked against previous experiments before transitioning to continuous flow experimentation, drastically shortening data collection wall-clock time to achieve a given sensitivity.

To test the capabilities of this instrument, the first target of experimentation was ethanol and water trimers. Once characterized, the cluster size of interest increased in accordance with the shortened timescale necessary for long averaging. Tetramers of neat ethanol, neat water, and mixed ethanol and water were observed next, showing formation of conformers with both microaggregation of water and ethanol and even mixing of the species in the tetramer. This trend was further explored in the study of all available planar pentamer conformers of neat and mixed methanol and water; fully interspersed clusters were not significantly different in energy or less favored in formation than conformers grouping water and methanol separately.

Further, this work with tetramers and pentamers raised the question as to the potential availability of higher cooperativity conformers as the cluster size increases. By switching to methanol in the study of pentamers, more direct comparison to pure water analogs could be drawn, as this is the smallest alcohol, limiting the steric effects of the carbon chain. This question was thus further explored by identifying pure methanol and mixed methanol and water hexamer conformers. From this study, a lack of preferential microaggregation was again observed. In addition, the observed hexamer conformers represented the tipping point between observing only planar conformations of mixed methanol and water clusters and observing three dimensional clusters following the hydrogen bond network pattern seen in neat water hexamers. These higher demensionality clusters correspond with higher net cooperativity as well, though the methanol monomer units in each conformer retained cooperativity = 2.

6.2 Future Directions

Looking beyond the study of these methanol and water hexamers, a number of future experimental directions will be explored. The first, and perhaps most obvious, is the natural extension of this work to study larger clusters and clusters of larger alcohols and water.

Formation of hexamers in the sample gas expansion carries some difficulties, particularly due to the relatively high vapor pressure of water compared to methanol. This difference led to much easier formation of pure methanol clusters, or clusters with a high ratio of methanol to water than formation of water-rich clusters. This discrepancy in turn increased the challenge of observing sufficient rotational states for water rich structures to fit them satisfactorily. In future experimentation, instrument modifications such as the implementation of a heated reservoir nozzle, or a switch back to pulsed gas expansion may be necessary to increase sensitivity to these larger clusters.

In addition, a full treatment of the internal rotation of methyl groups present in these large clusters of mixed alcohol and water would be a rich area for future study. The presence of multiple internal rotors makes the prediction of rotational state splitting nontrivial, and if this full fitting were completed in the future it would provide detailed insight into the large amplitude motion of these large clusters. In order to fit the full splitting due to internal rotation, a larger line list would be of use, so in this future work, even broader band spectra could be taken, and signal-to-noise on existing frequency ranges could be improved with longer averaging and potential optimization of expansion conditions. To facilitate formation of large clusters, the system could be switched back to a pulsed gas expansion mode, as the higher backing pressure for each pulse would help select for higher molecular weight clusters, though this would come at the cost of duty cycle and lab time spent per experiment.

Beyond the push towards larger clusters, studying larger alcohols such as propane and butane as they mix with water in small clusters may also be of interest. Comparing the behavior of these small clusters with that of the ethanol and water clusters studied herein could elucidate differences in bulk behavior for these species. In addition, these experiments would better inform the fine tuning of the unique force fields for molecular dynamics simulations of each type of alcohol and water mixture.

Another future direction for experimentation using the Blake group CPFTMW apparatus may move away from alcohol and water mixtures entirely, and instead incorporate a heated reservoir nozzle into the chamber for the study of sublimated solid samples. This instrumentation development would open up a whole new array of samples of interest that have never been characterized via CPFTMW. For example, many small aromatics of astrochemical interest like nitrophenols have not had precise conformational analysis, which would be of interest in understanding the reactivity of these species in space based chemistry on grain surfaces or giant molecular clouds. The Blake group instrument would be particularly well suited for these experiments given the high speed of data collection. This speed could be increased even more when studying monomers with high dipole moments, instead of the current targets of large clusters with low dipole moments. This increase would be due to the much higher signal to noise and cleaner spectrum obtained, as only monomers would be forming in abundance, instead of the currently typical raft of different cluster sizes and types.

If monomer analysis is in the near future, another potential improvement to the experimental set up would be the development of 'on the fly' data analysis instead of the lengthy post processing required for complex spectra. This would follow the program recently developed (Carroll, Lee, and McCarthy, 2021), in which spectra can be rapidly assigned and rotational constants at least preliminarily retrieved from rate data, removing the necessity of matching predicted lines to experimental data by hand. While additional fitting for splitting due to internal rotation or hyperfine splitting may be required, the incorporation of this rapid processing would allow for extremely fast simple rotational analysis, which would open the door for a number of collaborations without necessitating time intensive human resources or expensive instrument modification. For example, biochemists could retrieve structural data for small molecules of interest, improving modeling or drug development.

Finally, another area of future experimentation would be the implementation of dual resonance spectroscopy to probe the entirety of the potential energy surface for molecules or small clusters of interest. The intermolecular movement associated with hydrogen bond stretching lies in the terahertz energy regime, as discussed in the introduction, and this terahertz spectrum could be modulated by pinging the underlying rotational states of these terahertz transitions at the appropriate microwave frequency. The combination of these methods would allow for parsing apart the complex terahertz spectrum and ultimately recovering a more complete map of the potential energy surface of the small molecules or clusters of interest.

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Appendix A

SUPPLEMENTARY INFORMATION FOR CHAPTER 2

Supplemental Information for:
High Throughput Chirped Pulse Fourier-Transform Microwave Spectroscopy of Ethanol and Water Clusters
S. E. Dutton, G. A. Blake

First, the minima structures for pure ethanol trimers and mixed water and ethanol trimers were calculated with Gaussian to provide initial guesses at rotational constants. Here are the z-matrices of the minima on the potential energy surfaces used to predict these rotational constants and thus initially assign observed lines in the spectra.

Optimized ab initio equilibrium structures in PAS (MP2/aug-cc-pVTZ, tight convergence criteria):

Etoh Trimer Conformer 1

C	-1.9225890	-1.7325000	0.0015250
H	-2.8273200	-1.6920650	-0.6183830
H	-2.0931880	-1.1141830	0.8933880
O	-0.8054520	-1.2372250	-0.7349980
H	-0.9348710	-0.2810140	-0.8644370
H	0.8740620	-0.8682350	0.0418610
O	1.5418630	-0.2290240	0.3472120
O	-0.3974720	1.5222090	-0.5619080
H	0.4517340	1.1879530	-0.2231980
C	-0.9722420	2.3598250	0.4399450
H	-0.4189960	3.3056040	0.5005380
H	-0.9151220	1.8706430	1.4212340
C	-2.4177340	2.6228340	0.0637890
H	-2.9848200	1.6879290	0.0438120
H	-2.8852640	3.2972190	0.7872740
H	-2.4700640	3.0817710	-0.9267200
C	-1.6255370	-3.1635470	0.4051300
H	-2.4747140	-3.5929290	0.9447610
H	-1.4315770	-3.7707500	-0.4826110
H	-0.7461330	-3.2015350	1.0536340
C	2.8222930	-0.6348170	-0.1356100
H	3.1497230	-1.5404460	0.3904790
H	2.7667270	-0.8639710	-1.2072650
C	3.7989320	0.4983290	0.1117520
H	4.8043600	0.2138590	-0.2120370
H	3.4945430	1.3909940	-0.4410600
H	3.8306640	0.7407320	1.1770900

Etoh Trimer Conformer 2

C	2.8299410	0.6211640	-0.1253160

H	3.1551890	1.5167090	0.4190790
H	2.7896930	0.8669930	-1.1939530
O	1.5410970	0.2147700	0.3343670
H	0.8791390	0.8585420	0.0256700
H	0.4468030	-1.1949160	-0.2438270
O	-0.4065230	-1.5253910	-0.5759440
O	-0.7971570	1.2368650	-0.7522290
H	-0.9286900	0.2814490	-0.8859910
C	-1.9085210	1.7283410	-0.0040500
H	-2.0788350	1.0984830	0.8797980
H	-2.8160520	1.7019320	-0.6206100
C	-1.6005480	3.1516220	0.4186220
H	-1.4074980	3.7706170	-0.4612040
H	-2.4442240	3.5783670	0.9688700
H	-0.7175310	3.1747380	1.0629770
C	3.7967860	-0.5215130	0.1170800
H	4.8080800	-0.2381750	-0.1889430
H	3.8131150	-0.7807120	1.1788430
H	3.4943750	-1.4035880	-0.4535630
C	-0.9935500	-2.3272580	0.4481510
H	-0.4504940	-3.2764540	0.5392110
H	-0.9348330	-1.8095650	1.4147120
C	-2.4404380	-2.5859320	0.0742000
H	-2.9176860	-3.2341920	0.8150190
H	-2.9977050	-1.6461580	0.0251600
H	-2.4942040	-3.0725670	-0.9029260

Etoh:water tgg trimer

C	-2.0432630	-0.9802160	0.3234520
H	-1.9129420	-0.8262800	1.4026090
H	-1.8513900	-2.0387730	0.1065680
O	-1.1324430	-0.1612370	-0.4059880
H	-0.2366550	-0.3093340	-0.0530380
H	-0.7998450	1.7132000	-0.3170500
O	-0.1759480	2.4381480	-0.1394930
H	-0.7172780	3.1684760	0.1662320
O	1.4016060	0.2565380	0.6211480
H	1.1423580	1.1892590	0.5588840
C	2.6332350	0.0871790	-0.0832020
H	3.4492430	0.5635320	0.4740880
H	2.5698310	0.5613840	-1.0703810
C	2.8903790	-1.4001320	-0.2259370
H	2.0964850	-1.8693550	-0.8131990
H	3.8453610	-1.5756660	-0.7296050

H	2.9230720	-1.8723890	0.7592330
C	-3.4529780	-0.6100950	-0.0953140
H	-4.1829030	-1.2435510	0.4171640
H	-3.6645100	0.4334670	0.1529090
H	-3.5707800	-0.7419820	-1.1737460

Etoh:water gtt trimer

C	1.6598450	-1.0573680	0.0175120
H	1.5419260	-1.9986950	-0.5341150
H	1.0517950	-1.1188640	0.9304200
O	1.2273160	0.0369640	-0.7895770
H	0.2644530	-0.0473000	-0.9046790
H	0.9549840	1.7381490	-0.0350020
O	0.3711360	2.4205420	0.3415880
H	0.7577610	3.2567320	0.0733880
O	-1.5084120	0.5489740	-0.5606960
H	-1.1778270	1.4019060	-0.2370950
C	-2.3611860	-0.0040580	0.4416880
H	-3.3033550	0.5565630	0.4822520
H	-1.8819030	0.0652300	1.4267010
C	-2.6294800	-1.4530760	0.0841930
H	-1.6983740	-2.0266160	0.0831190
H	-3.3145720	-1.9048240	0.8074950
H	-3.0786550	-1.5174410	-0.9100440
C	3.1171000	-0.8372080	0.3734740
H	3.4963390	-1.6750430	0.9657680
H	3.7165770	-0.7517790	-0.5362650
H	3.2328600	0.0804080	0.9563340

bsequently, observed lines in the experimental data were fit using the rotational fitting program SPFIT. Here are the output
es from SPFIT detailing the fits for both ethanol trimers and the mixed ethanol water trimer, and providing the
perimentally derived rotational constants.

: output file for etoh trimer conformer 1

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
1:  6  5  1  5  4  1               10910.79000   10910.79008   -0.00008    0.10000   0.0
2:  6  6  0  5  5  0               11627.12000   11627.11871    0.00129    0.10000   0.0
3:  7  6  2  6  5  2               13008.84000   13008.83821    0.00179    0.10000   0.0
4:  7  5  3  6  4  3               12536.03000   12536.03807   -0.00807    0.10000   0.0
5:  10  2  9  9  1  8               10631.16000   10631.01296    0.14704    0.10000   0.0
6:  11  1 11 10  0 10                10725.00000   10725.02394   -0.02394    0.10000   0.00000
7:  11  2 10 10  1  9               11564.73000   11564.80233   -0.07233    0.10000   0.00000
8:  11  0 11 10  0 10                10725.00000   10725.02394   -0.02394    0.10000   0.00000
9:  11  1 10 10  1  9               11564.73000   11564.80166   -0.07166    0.10000   0.00000
.0:  12  2 10 11  2  9               13336.93000   13336.91241    0.01759    0.10000   0.00000   13336.91612    0.01388 0.5000
.1:  12  3 10 11  2  9               13336.93000   13336.91983    0.01017    0.10000   0.00000   13336.91612    0.01388 0.5000
.2:  13  0 13 12  0 12                12589.25000   12589.21074    0.03926    0.10000   0.00000
)RMALIZED DIAGONAL:
1  1.00000E+000   2  5.80616E-001   3  1.51421E-001   4  2.68086E-002   5  6.49455E-001   6  2.23798E-003
7  1.60213E-001   8  9.96703E-001
ARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
.       10000        A        996.292( 39)        -0.000
!       20000        B        802.643(103)         0.000
}       30000        C       469.3070(208)        -0.0000
I         200    -DeltaJ       -0.01512( 92)       -0.00000
;         2000    -DeltaK       -0.03642(235)        -0.00000
;         1100   -DeltaJK         0.0476( 33)         0.0000
'       40100    -deltaJ          -4.54( 41)E-03       -0.00E-03
}       41000    -deltaK        -0.03777(240)        -0.00000
ICROWAVE AVG =       0.000295 MHz, IR AVG =       0.00000
ICROWAVE RMS =       0.056357 MHz, IR RMS =       0.00000
```

: output file for etoh trimer conformer 2

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
1:  6  2  4  5  1  4               11079.90000   10541.58793   -0.01793    0.10000   0.00000
2:  6  5  1  5  4  1               11079.90000   11079.90737   -0.00737    0.10000   0.00000
3:  7  5  3  6  4  3               12674.75000   12674.74116    0.00884    0.10000   0.00000
4:  7  7  1  6  6  1               13877.77000   13877.76912    0.00088    0.10000   0.00000
5:  8  4  4  7  3  4               13671.07000   13671.06385    0.00615    0.10000   0.00000
6:  10  1  9  9  1  8               10726.75000   10726.62307    0.12693    0.10000   0.00000   10726.62898    0.12102 0.5000
```

```
7:  10  2  9  9  1  8              10726.75000   10726.63489    0.11511    0.10000   0.00000   10726.62898    0.12102 0.5000
8:  12  0 12 11  0 11              11770.86000   11771.06972   -0.20972    0.10000   0.00000   11771.06972   -0.20972 0.5000
9:  12  1 12 11  0 11              11770.86000   11771.06972   -0.20972    0.10000   0.00000   11771.06972   -0.20972 0.5000
.0:  12  2 10 11  2  9             13451.06000   13451.09248   -0.03248    0.10000   0.00000   13451.10545   -0.04545 0.5000
.1:  12  3 10 11  2  9             13451.06000   13451.11842   -0.05842    0.10000   0.00000   13451.10545   -0.04545 0.5000
.2:  13  0 13 12  0 12             12710.80000   12710.65455    0.14545    0.10000   0.00000   12710.65455    0.14545 0.5000
.3:  13  1 13 12  0 12             12710.80000   12710.65455    0.14545    0.10000   0.00000   12710.65455    0.14545 0.5000
ORMALIZED DIAGONAL:
1  1.00000E+000    2  9.20466E-001    3  1.43256E-001    4  4.29959E-002    5  9.97594E-001    6  1.30929E-002
7  2.56916E-001    8  6.91615E-001
ARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
.       10000        A        1012.484( 45)          -0.000
2       20000        B        800.3553(215)          -0.0000
3       30000        C        474.2770(177)          -0.0000
4         200    -DeltaJ          1.311(171)E-03        0.000E-03
5        2000    -DeltaK        -0.04117( 60)        -0.00000
6        1100    -DeltaJK         0.03553( 64)         0.00000
7       40100     -deltaJ       -0.013783(161)       -0.000000
8       41000     -deltaK        -0.07710(100)        -0.00000
ICROWAVE AVG =       0.000207 MHz, IR AVG =        0.00000
ICROWAVE RMS =       0.095651 MHz, IR RMS =        0.00000

----------------------------------------------------------------------------------------------------------------

: output file for etoh:water tgg


                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
1:   5  5  0  5  4  2             16952.56000   16952.56024   -0.00024    0.10000   0.00000
2:   6  1  6  5  0  5             10000.00000   10000.09745   -0.09745    0.10000   0.00000
3:   6  2  5  5  1  5             17017.81000   17017.80514    0.00486    0.10000   0.00000
4:   7  0  7  6  0  6             10864.80000   10864.60872    0.19128    0.10000   0.00000
5:   8  1  8  7  1  7             12158.19000   12158.45061   -0.26061    0.10000   0.00000
6:   8  0  8  7  0  7             12294.80000   12294.60843    0.19157    0.10000   0.00000
7:   8  2  7  7  2  6             12995.00000   12995.03937   -0.03937    0.10000   0.00000
8:  10  7  3  9  7  2             16552.69000   16552.68880    0.00120    0.10000   0.00000
9:  11  1 10 10  2  9              16510.92000   16510.92576   -0.00576    0.10000   0.00000
.0:  11  1 10 10  1  9             18049.24000   18049.22768    0.01232    0.10000   0.00000
ORMALIZED DIAGONAL:
1  1.00000E+000    2  4.57104E-001    3  6.18592E-001    4  9.99985E-001    5  1.47089E-001    6  7.50179E-003
7  1.77235E-001    8  8.16859E-001
ARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
```

```
      10000        A        2709.384( 71)          0.000
      20000        B        923.4670(172)         -0.0000
      30000        C        724.8563(133)         -0.0000
        200    -DeltaJ       0.02092( 87)        -0.00000
       2000    -DeltaK        0.03112(171)        -0.00000
       1100    -DeltaJK      -0.05419(262)         0.00000
      40100     -deltaJ      -0.01409( 54)         0.00000
      41000     -deltaK       0.02243(117)         0.00000
ICROWAVE AVG =      -0.000221 MHz, IR AVG =       0.00000
ICROWAVE RMS =       0.117729 MHz, IR RMS =       0.00000
------------------------------------------------------------------------------------------------------------------
 output file for etoh:water gtt conformer


                          EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
1:  4  0  4  3  0  3                  7203.91000   7203.89052    0.01948    0.10000   0.00000
2:  4  4  1  3  3  1                 17846.51000  17846.51296   -0.00296    0.10000   0.00000
3:  5  3  3  4  2  3                 16969.86000  16969.85142    0.00858    0.10000   0.00000
4:  6  2  5  5  2  4                 11125.22000  11125.25282   -0.03282    0.10000   0.00000
5:  6  1  6  5  0  5                 10644.92000  10645.08746   -0.16746    0.10000   0.00000
6:  7  1  7  6  0  6                 12145.17000  12144.99517    0.17483    0.10000   0.00000
7:  9  1  8  8  1  7                 16722.44000  16722.43037    0.00963    0.10000   0.00000
8:  10  2  9  9  1  8                 18681.93000  18681.93237   -0.00237    0.10000   0.00000
9:  11  1 11 10  1 10                 18446.03000  18446.04765   -0.01765    0.10000   0.00000
RMALIZED DIAGONAL:
1  1.00000E+000   2  7.78186E-001   3  3.67944E-001   4  2.52601E-002   5  6.56557E-001   6  1.24807E-003
7  9.99925E-001   8  2.31431E-001
ARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
      10000        A         2406.62( 32)           0.00
      20000        B        1068.142( 73)          0.000
      30000        C        810.0104(162)         -0.0000
        200    -DeltaJ         0.1517( 64)        -0.0000
       2000    -DeltaK          0.1359( 65)        -0.0000
       1100    -DeltaJK        -0.2891(129)         0.0000
      40100     -deltaJ      -0.05870(255)         0.00000
      41000     -deltaK       0.02981(211)        -0.00000
ICROWAVE AVG =      -0.001192 MHz, IR AVG =       0.00000
ICROWAVE RMS =       0.082029 MHz, IR RMS =       0.00000
```

Error in the fitted rotational constants from SPFIT was anomalously high, so potential splitting of the observed rotational states due to internal rotation was examined. The XIAM program was used to fit the splitting of rotational states due to internal rotation of the methyl groups present in the ethanol trimers and mixed ethanol water trimers. Here is example output from the XIAM file for fitting two non-equivalent rotors of the ethanol trimer (conformer 1):

Example of XIAM line fitting:Etoh Conformer 1

```
   J K- K+  J K- K+    Sym   calc/GHz  Sign of Difference
  1:  6  6  0  5  5  0   S 0  11.5445950   +
  2:  7  5  3  6  4  3   S 0  12.5376614   -
  3:  7  6  1  6  5  1   S 0  12.8606900   +
  4:  7  7  1  6  6  1   S 0  13.4838409   +
  5: 10  2  9  9  1  8   S 0  10.7223401   +
  6: 11  1 11 10  0 10   S 0  10.8657453   -
  7: 11  0 11 10  0 10   S 0  10.8657453   -
  8: 12  2 10 11  2  9   S 0  13.4833227   -
  9: 12  3 10 11  2  9   S 0  13.4833234   -
 10: 13  0 13 12  0 12   S 0  12.8274753   -
```

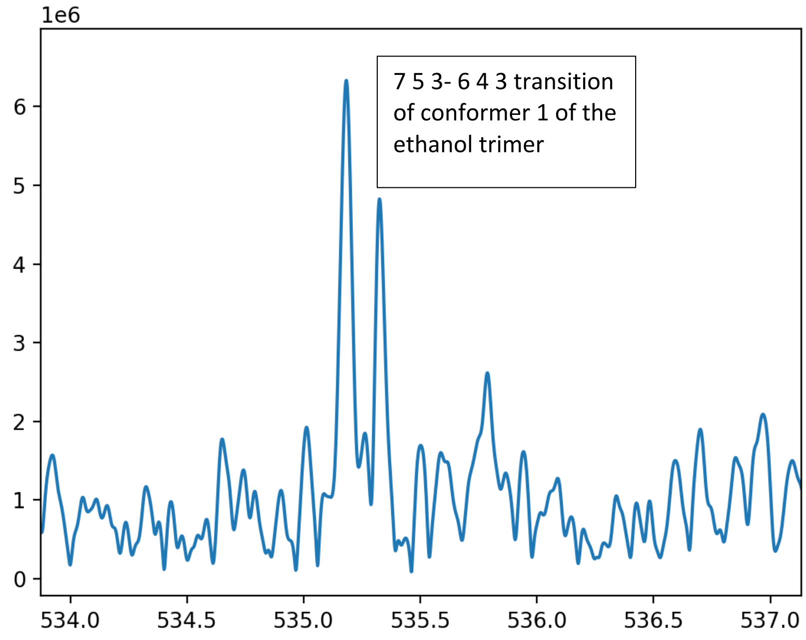
Examples of XIAM output lines in Ethanol trimer; note that the magnitude of splitting is not large enough to resolve with this instrument, but large enough to contribute to the error observed in the SPFIT results.

```
13  0 13  12  0 12   S 1  V 1   12.827487   6.5071   .0000  25.0000   .0000   .0597  B 1  K  0  0  t  1  1
13  1 13  12  0 12   S 1  V 1   12.827487  10.9999   .0000  25.0000   .0000   .0597  B 1  K -1  0  t  2  1

13  0 13  12  0 12   S 2  V 1   12.827481  17.5070   .0000  25.0000   .0000   .0597  B 1  K  0  0  t  1  1
13  1 13  12  1 12   S 2  V 1   12.827492  17.5070   .0000  25.0000   .0000   .0597  B 1  K  0  0  t  2  2

13  0 13  12  0 12   S 4  V 1   12.827475  17.5069   .0000  25.0000   .0000   .0597  B 1  K  0  0  t  1  1
13  1 13  12  1 12   S 4  V 1   12.827497  17.5070   .0000  25.0000   .0000   .0597  B 1  K  0  0  t  2  2

13  0 13  12  0 12   S 5  V 1   12.827486   3.3411   .0000  25.0000   .0000   .0597  B 1  K  0  0  t  1  1
13  1 13  12  0 12   S 5  V 1   12.827486  14.1659   .0000  25.0000   .0000   .0597  B 1  K -1  0  t  2  1

 9  9  0   8  8  0   S 1  V 1   17.277052    .7850   .0000  17.0000   .0000   .0796  B 1  K  9  8  t 19 17
 9  9  0   8  8  0   S 2  V 1   17.277118   6.0942   .0000  17.0000   .0000   .0796  B 1  K -9 -8  t 19 17
 9  9  0   8  8  0   S 3  V 1   17.277118   6.0942   .0000  17.0000   .0000   .0796  B 1  K -9 -8  t 19 17
 9  9  0   8  8  0   S 4  V 1   17.277189   9.2181   .0000  17.0000   .0000   .0796  B 1  K -9 -8  t 19 17
 9  9  0   8  8  0   S 5  V 1   17.277046    .7850   .0000  17.0000   .0000   .0796  B 1  K  9  8  t 19 17
```

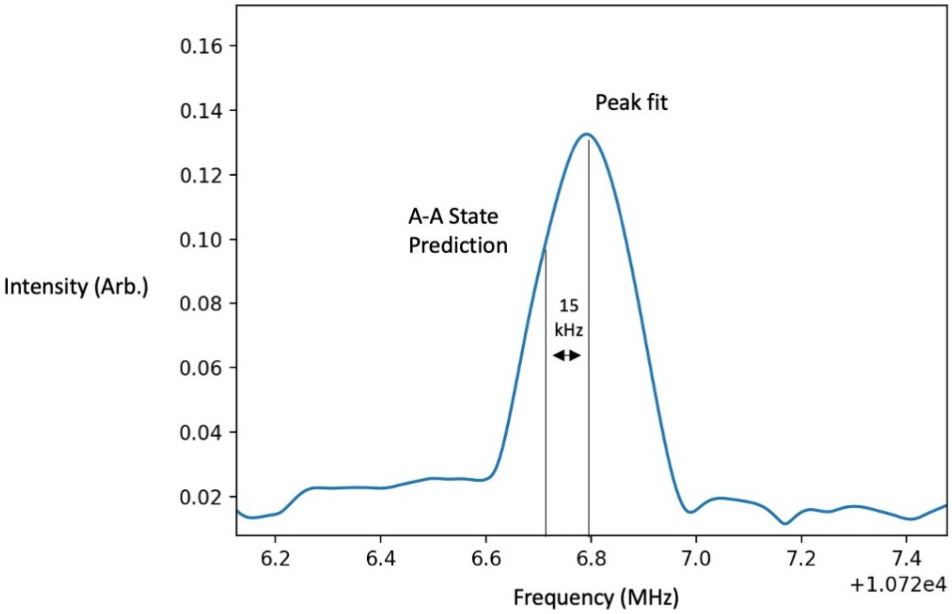
```
10  1  9   9  1  8   S 1  V 1   10.722346   .1731   .0000  19.0000   .0000   .0502  B 1  K  3  3  t  3  3
10  1  9   9  1  8   S 3  V 1   10.722337  11.5551   .0000  19.0000   .0000   .0502  B 1  K  3  3  t  3  3
10  1  9   9  1  8   S 4  V 1   10.722331  11.5747   .0000  19.0000   .0000   .0502  B 1  K  3  3  t  3  3
10  1  9   9  1  8   S 5  V 1   10.722345   .1731   .0000  19.0000   .0000   .0502  B 1  K  3  3  t  3  3


12  0 12  11  0 11   S 1  V 1   11.842965   1.0817   .0000  23.0000   .0000   .0553  B 1  K  0  0  t  1  1
12  0 12  11  0 11   S 2  V 1   11.842959  16.0887   .0000  23.0000   .0000   .0553  B 1  K  0  0  t  1  1
12  0 12  11  0 11   S 3  V 1   11.842959  16.0887   .0000  23.0000   .0000   .0553  B 1  K  0  0  t  1  1
12  0 12  11  0 11   S 4  V 1   11.842953  16.0887   .0000  23.0000   .0000   .0553  B 1  K  0  0  t  1  1
12  0 12  11  0 11   S 5  V 1   11.842965   .5142   .0000  23.0000   .0000   .0553  B 1  K  0  0  t  1  1
```

The fitting from XIAM was supported by the asymmetry of the peaks when resolved with long (~50us) FID collection. Here is one such peak, with asymmetry in both shape and doppler split peaks apparent. This line is the 7 5 3- 6 4 3 transition of conformer 1 of the ethanol trimer.

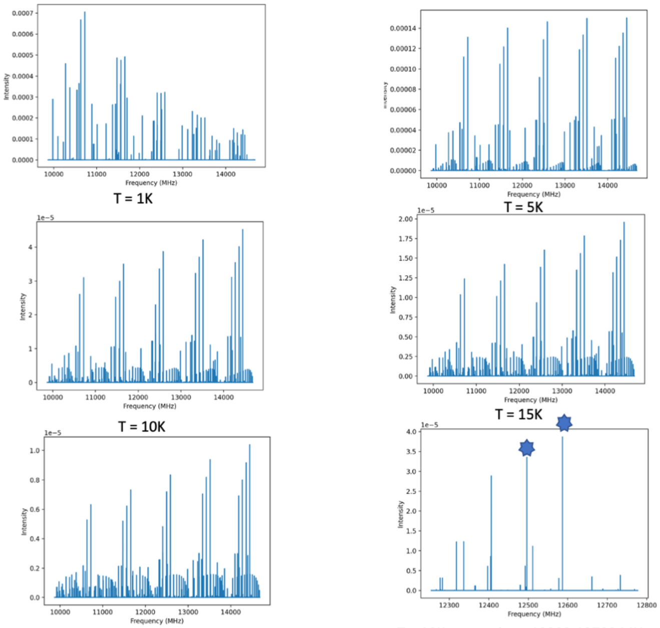
Asymmetry of line at 12536 MHz:



In addition, XIAM predictions of error were compared to peaks fit, to show that with increased sensitivity to fit only the AA states, error in spfit would follow expected experimental error on the order of ~10s of kHz. For example, this peak at 10726 MHZ for conformer 2 of the ethanol trimer has a predicted AA state position ~15 kHz less than the EA state position. This additional error is represented in the image below. Other peaks fit have predicted error from XIAM ranging from 5 to 100 kHz. Were we able to fit the peak positions of the AA states precisely, the total spfit error for this conformer would be ~40 kHz, closer to the expected value.



Finally, rotational temperature of the experimental expansion was approximated by comparison to spectra simulated with the program PGOPHER. Here is a comparison of simulated spectra at different temperatures with real data, used to assign the approximate rotational temperature of the supersonic expansion. Note that only a-type modes are presented in the simulated spectra, limiting the comparison, but the shape of the Boltzmann distribution for all states was compared to data to yield a best-guess at rotational temperature.



T = 1K

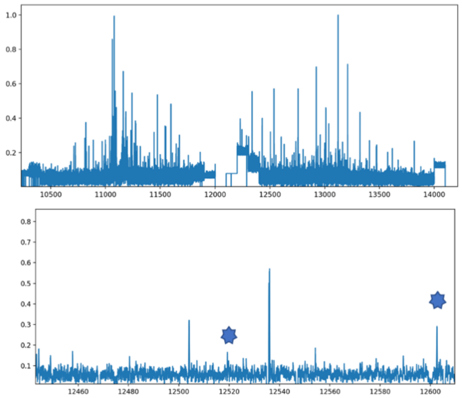
T = 5K

T = 10K

T = 15K

T = 20K

T = 10K—zoom in to 12300-12700 MHz



Total ethanol spectrum with monomer lines removed, above, and detail at ~12500 MHz showing relative peak intensity, below.

Relative intensity of observed trimer peaks matches profile for T > 5 K, but <15 K (note scale changes for each plot). Thus, rotational energy of expansion is ~10 K.

Appendix B

SUPPLEMENTARY INFORMATION FOR CHAPTER 3

Supplementary Information for: “Chirped Pulse Fourier-Transform Microwave Spectroscopy of Alcohol and Water Tetramers”

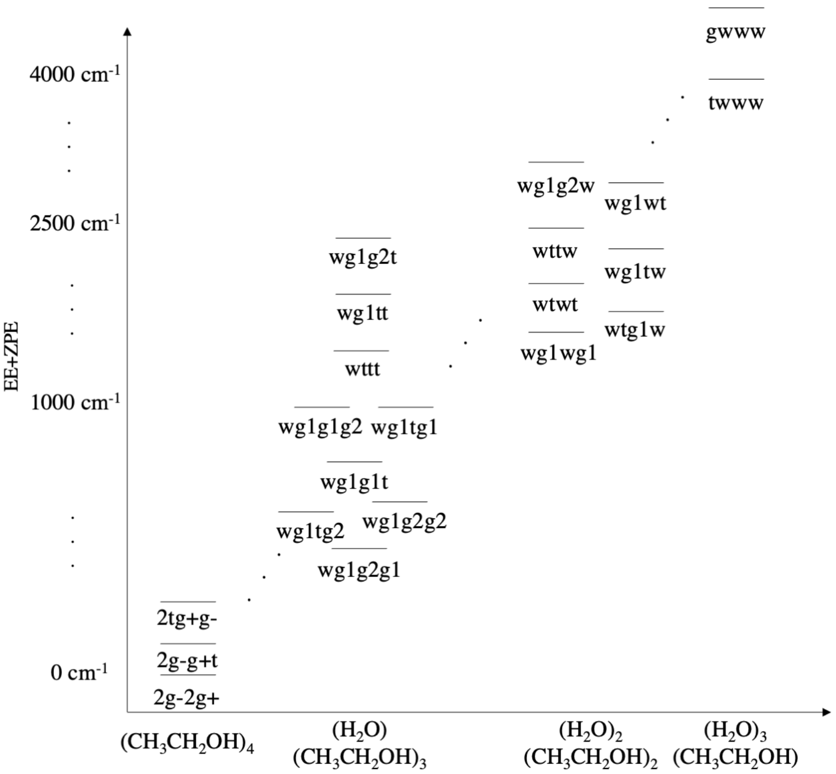
In this supplementary information, the authors include details on computational modeling and spectroscopic fits for ethanol:water tetramers. The sections are listed below, and brief descriptions of each section are included.

Sections:

1. Relative Energy Ordering of all Optimized Tetramer Conformers
2. SPFIT Results
3. Kraitchman Substitution results and calculated O-O distances
4. Images of fitted conformers
5. Sample XIAM results

Section 1: Relative Energy Ordering of all Optimized Tetramer Conformers

Herein is included a figure demonstrating the relative energy of all tetramer conformers optimized via *ab initio* computation. Each conformer geometry was optimized with DFT in Gaussian at the B3LYP level of theory and the 6-311G++(d,p) basis set. Energy of tetramer conformers is increased with addition of water, as shown on the horizontal axis. Energy differences between conformers with a set number of water molecules are small, at less than 400 cm-1. This implies the potential presence of all conformers in experimental expansions, limiting detection of conformers to the dipole moment of each structure.



Relative energy ordering of ethanol:water tetramers investigated herein, expressed as electronic energy (EE) plus zero point correction (ZPE). Gaps between groupings of conformers are on the order of several hundred wavenumbers, while gaps between conformers with the same number of water/ethanol subunits are on the order of 1000s of wavenumbers, as seen in previous studies (Nishi, 1988}. Relative energies between conformers of the same hydration level calculated with Gaussian using B3LYP/6311g++(d,p).

Section 2: SPFIT results for ethanol:water tetramers and their isotopologues

In this section, SPFIT output files are included for all tetramer conformers observed in the experimental data, as well as perdeuterated isotopologues and singly deuterated isotopologues. Files are organized by number of water molecules, with all ethanol tetramer fits first, then one-water tetramers, etc. Each fit is separated by a page break.

SPFIT Details for 2tg+g-

```
                              EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  10 10  1  9  9  0              10968.73000   10968.72511    0.00489    0.10000   0.00000
   2:  11  2 10 10  1  9              10453.03000   10453.07030   -0.04030    0.10000   0.00000
   3:  12 12  0 11 11  0              13170.46000   13170.46486   -0.00486    0.10000   0.00000
   4:  13  0 13 12  0 12              12158.16000   12158.21198   -0.05198    0.10000   0.00000
   5:  13  1 12 12  1 11              12306.68000   12306.64881    0.03119    0.10000   0.00000
   6:  13  1 13 12  0 12              12158.16000   12158.21198   -0.05198    0.10000   0.00000
   7:  13  2 12 12  1 11              12306.68000   12306.64881    0.03119    0.10000   0.00000
   8:  17 17  1 16 16  1              18665.48000   18665.47884    0.00116    0.10000   0.00000
   9:  18  0 18 17  0 17              16803.55000   16803.41026    0.13974    0.10000   0.00000
  10:  18  5 14 17  4 13              17402.21000   17402.21651   -0.00651    0.10000   0.00000
  11:  19  1 19 18  0 18              17732.57000   17732.48319    0.08681    0.10000   0.00000
17732.48319    0.08681 0.5000
  12:  19  1 19 18  1 18              17732.57000   17732.48319    0.08681    0.10000   0.00000
17732.48319    0.08681 0.5000
  13:  20  0 20 19  1 19              18661.40000   18661.55364   -0.15364    0.10000   0.00000
18661.55364   -0.15364 0.5000
  14:  20  0 20 19  0 19              18661.40000   18661.55364   -0.15364    0.10000   0.00000
18661.55364   -0.15364 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  8.18444E-001    3  3.66147E-001    4  4.78148E-002    5  9.98447E-001
6  4.05199E-003
   7  1.06679E-001    8  2.95007E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                       NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1       10000        A          550.825( 56)          0.000
   2       20000        B          539.159(216)          0.001
   3       30000        C         464.6791(134)         -0.0000
   4         200    -DeltaJ     -0.012301(228)        -0.000001
   5        2000    -DeltaK      -0.027735(216)        -0.000001
   6        1100    -DeltaJK       0.03944( 48)         0.00000
   7       40100     -deltaJ       -9.687( 78)E-03       0.000E-03
   8       41000     -deltaK       0.02668(156)        -0.00000
```

```
MICROWAVE AVG =     -0.001189 MHz, IR AVG =       0.00000
         MICROWAVE RMS =       0.070553 MHz, IR RMS =       0.00000
```

SPFIT Details for all ethanol-d6 2tg+g-

```
                      EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  18  0 18 17  0 17              14254.99000   14254.98241    0.00759    0.10000   0.09386
14254.98241    0.00759 0.5000
   2:  18  1 18 17  0 17              14254.99000   14254.98241    0.00759    0.10000   0.09386
14254.98241    0.00759 0.5000
   3:  19  2 18 18  2 17              15156.32000   15156.35680   -0.03680    0.10000   0.05833
15156.35680   -0.03680 0.5000
   4:  19  1 18 18  2 17              15156.32000   15156.35680   -0.03680    0.10000   0.05833
15156.35680   -0.03680 0.5000
   5:  19  2 17 18  2 16              15271.57000   15271.55459    0.01541    0.10000   0.08660
15271.55460    0.01540 0.5000
   6:  19  3 17 18  2 16              15271.57000   15271.55462    0.01538    0.10000   0.08660
15271.55460    0.01540 0.5000
   7:  21  1 21 20  1 20              16622.48000   16622.45103    0.02897    0.10000   0.09580
16622.45103    0.02897 0.5000
   8:  21  0 21 20  1 20              16622.48000   16622.45103    0.02897    0.10000   0.09580
16622.45103    0.02897 0.5000
   9:  21  2 20 20  2 19              16732.27000   16732.36371   -0.09371    0.10000   0.05195
16732.36371   -0.09371 0.5000
  10:  21  1 20 20  2 19              16732.27000   16732.36371   -0.09371    0.10000   0.05195
16732.36371   -0.09371 0.5000
  11:  21  2 19 20  2 18              16846.32000   16846.11733    0.20267    0.10000   0.06113
16846.11733    0.20267 0.5000
  12:  21  3 19 20  2 18              16846.32000   16846.11733    0.20267    0.10000   0.06113
16846.11733    0.20267 0.5000
  13:  21  3 18 20  3 17              16962.14000   16962.27891   -0.13891    0.10000   0.07581
16962.27893   -0.13893 0.5000
  14:  21  4 18 20  3 17              16962.14000   16962.27895   -0.13895    0.10000   0.07581
16962.27893   -0.13893 0.5000
  15:  21  4 17 20  4 16              17080.19000   17080.15778    0.03222    0.10000   0.09618
  16:  22  2 21 21  2 20              17520.26000   17520.27753   -0.01753    0.10000   0.07617
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  1.13449E-002    3  1.02445E-001    4  6.50228E-004    5  7.22510E-001
6  2.50223E-005
   7  2.61584E-002    8  1.82523E-001
MARQUARDT PARAMETER = 7.18784e-005, TRUST EXPANSION = 1.00
                   NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A          492.24(111)           0.00
   2        20000         B          430.90( 43)          -0.00
   3        30000         C        394.1888(157)         -0.0000
   4          200    -DeltaJ      0.020343( 98)       -0.000000
   5         2000     -DeltaK      0.026990(117)        -0.000000
   6         1100    -DeltaJK        -0.047647(113)         0.000001
```

```
  7        40100    -deltaJ         -0.013376(228)         0.000000
  8        41000    -deltaK          0.02357( 34)         -0.00000
MICROWAVE AVG =       -0.000013 MHz, IR AVG =        0.00000
MICROWAVE RMS =        0.090056 MHz, IR RMS =        0.00000
```

SPFIT Details for wg1g2t

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   8  3  6  7  2  6               11079.94000   11079.94014   -0.00014    0.10000   0.00000
   2:   9  2  8  8  1  8               12443.43000   12443.43003   -0.00003    0.10000   0.00000
   3:  11  2  9 10  2  8                10153.98000   10153.97929    0.00071    0.10000   0.00000
   4:  11  5  7 10  5  6                10429.67000   10429.66996    0.00004    0.10000   0.00000
   5:  13  0 13 12  0 12                  10260.36000   10260.30444    0.05556    0.10000   0.00000
   6:  13  1 13 12  0 12                  10260.39000   10260.44598   -0.05598    0.10000   0.00000
   7:  21  3 19 20  2 18                  17658.59000   17658.59034   -0.00034    0.10000   0.00000
   8:  22  1 22 21  0 21                  17132.56000   17132.56524   -0.00524    0.10000   0.00000
   9:  22  0 22 21  0 21                  17132.57000   17132.56480    0.00520    0.10000   0.00000
  10:  23  2 22 22  1 21                   18536.55000   18536.54970    0.00030    0.10000   0.00000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  4.80270E-001    3  9.96601E-001    4  5.95483E-003    5  3.27645E-001
6  3.20074E-004
   7  6.15607E-001    8  9.51515E-002
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1         10000          A         1036.863(157)            0.000
   2         20000          B          538.362( 48)           -0.000
   3         30000          C         381.6686(165)          -0.0000
   4           200    -DeltaJ            -2.14( 82)E-03        -0.00E-03
   5          2000    -DeltaK          -0.1883( 33)           -0.0000
   6          1100   -DeltaJK            0.1904( 41)           0.0000
   7         40100     -deltaJ       -0.024522(242)         -0.000000
   8         41000     -deltaK         -0.09823(156)          -0.00000
 MICROWAVE AVG =        0.000006 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.025052 MHz, IR RMS =        0.00000
```

SPFIT Details for wg1g2t with d2o

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  6  6  1  5  5  1              11530.89000  11530.88973   0.00027   0.10000   0.07071
   2:  6  6  1  5  5  1              11530.89000  11530.88973   0.00027   0.10000   0.07071
   3:  8  8  1  7  7  1              15554.70000  15554.70112  -0.00112   0.10000   0.09999
   4:  9  8  2  8  7  2              16478.62000  16478.61912   0.00088   0.10000   0.10000
   5:  15  2 13 14  2 12               12937.50000  12937.51295  -0.01295   0.10000   0.09964
   6:  17  0 17 16  0 16               13156.03000  13156.03922  -0.00922   0.10000   0.09970
13156.03948   -0.00948 0.5000
   7:  17  1 17 16  0 16               13156.03000  13156.03974  -0.00974   0.10000   0.09970
13156.03948   -0.00948 0.5000
   8:  18  1 17 17  1 16               14546.90000  14546.79699   0.10301   0.10000   0.06915
14546.80464    0.09536 0.5000
   9:  18  2 17 17  1 16               14546.90000  14546.81229   0.08771   0.10000   0.06915
14546.80464    0.09536 0.5000
   10:  19  1 18 18  1 17               15300.50000  15300.58624  -0.08624   0.10000   0.07372
15300.58907   -0.08907 0.5000
   11:  19  2 18 18  1 17               15300.50000  15300.59191  -0.09191   0.10000   0.07372
15300.58907   -0.08907 0.5000
   12:  20  2 18 19  2 17               16695.96000  16695.90700   0.05300   0.10000   0.09973
16695.95118    0.00882 0.5000
   13:  20  3 18 19  2 17               16695.96000  16695.99536  -0.03536   0.10000   0.09973
16695.95118    0.00882 0.5000
   14:  22  0 22 21  0 21               16924.50000  16924.49286   0.00714   0.10000   0.09989
16924.49286    0.00714 0.5000
   15:  22  1 22 21  0 21               16924.50000  16924.49286   0.00714   0.10000   0.09989
16924.49286    0.00714 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  2.72255E-001   3  1.46898E-001   4  1.24383E-002   5  6.45289E-001
6  2.07548E-003
   7  1.06209E-001   8  9.99424E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                       NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A       1006.2347(168)          0.0000
   2        20000          B        537.470(122)          -0.000
   3        30000          C        377.8764(111)          0.0000
   4          200    -DeltaJ           -1.606(212)E-03        0.000E-03
   5         2000     -DeltaK            -9.80( 63)E-03       -0.00E-03
   6         1100    -DeltaJK        0.01185( 80)          0.00000
   7        40100     -deltaJ           -1.089(116)E-03        0.000E-03
   8        41000     -deltaK            -5.63( 45)E-03       -0.00E-03
 MICROWAVE AVG =        0.000013 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.041732 MHz, IR RMS =        0.00000
```

SPFIT Details for wg1g2t with HDO

```
                          EXP.FREQ.  - CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  6  0  5  5  1             11783.46000   11783.46730   -0.00730    0.10000   0.00000
11783.46532   -0.00532 0.5000
   2:   6  6  1  5  5  1             11783.46000   11783.46333   -0.00333    0.10000   0.00000
11783.46532   -0.00532 0.5000
   3:   8  7  2  7  6  2             14771.87000   14771.86984    0.00016    0.10000   0.00000
   4:   8  8  1  7  7  1             15900.84000   15900.83795    0.00205    0.10000   0.00000
   5:  15  2 13 14  2 12               13053.14000   13052.90749    0.23251    0.10000   0.00000
   6:  17  0 17 16  0 16               13279.98000   13280.06186   -0.08186    0.10000   0.00000
   7:  17  3 15 16  2 14               14567.55000   14567.76733   -0.21733    0.10000   0.00000
   8:  21  1 20 20  1 19               16965.84000   16965.73323    0.10677    0.10000   0.00000
16965.73440    0.10560 0.5000
   9:  21  2 20 20  1 19               16965.84000   16965.73557    0.10443    0.10000   0.00000
16965.73440    0.10560 0.5000
  10:  22  0 22 21  0 21               17085.92000   17085.94749   -0.02749    0.10000   0.00000
17085.94749   -0.02749 0.5000
  11:  22  1 22 21  0 21               17085.92000   17085.94750   -0.02750    0.10000   0.00000
17085.94749   -0.02749 0.5000
  12:  24  2 23 24  1 24               14822.16000   14822.16513   -0.00513    0.10000   0.00000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  4.62457E-002    3  2.24027E-001    4  9.95545E-001    5  1.93706E-003
6  1.25979E-002
   7  9.24369E-001    8  2.49410E-002
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                        NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1         10000          A        1028.7704(225)          -0.0000
   2         20000          B          539.141( 48)          -0.000
   3         30000          C         381.3754( 75)          -0.0000
   4           200    -DeltaJ          -3.864(171)E-03       -0.000E-03
   5          2000    -DeltaK            -7.85( 62)E-03       -0.00E-03
   6          1100    -DeltaJK          0.01133( 75)          0.00000
   7         40100     -deltaJ         -3.087( 91)E-03       -0.000E-03
   8         41000     -deltaK            1.09( 38)E-03       -0.00E-03
 MICROWAVE AVG =        0.000355 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.115452 MHz, IR RMS =        0.00000
```

SPFIT Details for wttt

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  6  1  5  5  1              11251.03000   11251.03001   -0.00001    0.10000   0.07071
   2:   6  6  1  5  5  1              11251.03000   11251.03001   -0.00001    0.10000   0.07071
   3:   7  7  1  6  6  1              13214.40000   13214.39999    0.00001    0.10000   0.10000
   4:  14  0 14 13  0 13                 10268.40000   10268.43077   -0.03077    0.10000   0.06333
   5:  14  1 13 13  1 12                 10931.92000   10931.91253    0.00747    0.10000   0.09942
   6:  14  1 14 13  0 13                 10268.40000   10268.43735   -0.03735    0.10000   0.06329
   7:  16  0 16 15  0 15                 11685.37000   11685.27693    0.09307    0.10000   0.05236
11685.27735    0.09265 0.5000
  8:  16  1 16 15  0 15                11685.37000   11685.27776    0.09224    0.10000   0.05236
11685.27735    0.09265 0.5000
  9:  18  1 17 17  1 16                13764.26000   13764.26345   -0.00345    0.10000   0.10133
13764.26810   -0.00810 0.5000
  10:  18  2 17 17  1 16                 13764.26000   13764.27276   -0.01276    0.10000   0.10133
13764.26810   -0.00810 0.5000
  11:  19  0 19 18  0 18                 13808.25000   13808.27805   -0.02805    0.10000   0.09682
13808.27807   -0.02807 0.5000
  12:  19  1 19 18  0 18                 13808.25000   13808.27809   -0.02809    0.10000   0.09682
13808.27807   -0.02807 0.5000
  13:  24  2 22 23  2 21                 18667.30000   18667.29996    0.00004    0.10000   0.10006
  14:  24  1 23 23  1 22                 18004.43000   18004.42788    0.00212    0.10000   0.09858
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  2.47276E-001    3  5.82286E-001    4  4.95142E-003    5  1.25254E-001
6  2.77648E-004
   7  3.82011E-002    8  9.97532E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1         10000          A          982.109( 33)           0.000
   2         20000          B          528.576(169)          -0.000
   3         30000          C        355.1998(100)           0.0000
   4           200    -DeltaJ            -5.74( 50)E-03         0.00E-03
   5          2000     -DeltaK          -0.0237( 42)          0.0000
   6          1100    -DeltaJK           0.0286( 46)         -0.0000
   7         40100     -deltaJ          -1.343(172)E-03        0.000E-03
   8         41000     -deltaK         -0.01263(301)          0.00000
 MICROWAVE AVG =       -0.000183 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.032809 MHz, IR RMS =        0.00000
```

SPFIT Details for wttt with d2o

```
                        EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  6  6  1  5  5  1              10951.02000  10951.02026  -0.00026    0.10000   0.00000
   2:  6  6  1  5  5  1              10951.02000  10951.02026  -0.00026    0.10000   0.00000
   3:  9  8  2  8  7  2              15668.49000  15668.48970   0.00030    0.10000   0.00000
  4:  20  1 19 19  1 18                15019.45000  15019.32347    0.12653    0.10000   0.00000
15019.32359    0.12641 0.5000
  5:  20  2 19 19  1 18                15019.45000  15019.32371    0.12629    0.10000   0.00000
15019.32359    0.12641 0.5000
  6:  20  2 18 19  2 17                15681.13000  15681.18762   -0.05762    0.10000   0.00000
  7:  20  3 18 19  2 17                15681.14000  15681.20028   -0.06028    0.10000   0.00000
  8:  20  3 17 19  3 16                16348.80000  16348.58534    0.21466    0.10000   0.00000
16348.77732    0.02268 0.5000
  9:  20  4 17 19  3 16                16348.80000  16348.96930   -0.16930    0.10000   0.00000
16348.77732    0.02268 0.5000
  10:  21  0 21 20  0 20                 15058.94000  15059.01345   -0.07345    0.10000   0.00000
15059.01345   -0.07345 0.5000
  11:  21  1 21 20  0 20                 15058.94000  15059.01345   -0.07345    0.10000   0.00000
15059.01345   -0.07345 0.5000
  12:  22  2 20 21  2 19                 17079.71000  17079.67081    0.03919    0.10000   0.00000
17079.67155    0.03845 0.5000
  13:  22  3 20 21  2 19                 17079.71000  17079.67230    0.03770    0.10000   0.00000
17079.67155    0.03845 0.5000
  14:  22  3 19 21  3 18                 17744.01000  17743.96607    0.04393    0.10000   0.00000
17743.99225    0.01775 0.5000
  15:  22  4 19 21  3 18                 17744.01000  17744.01844   -0.00844    0.10000   0.00000
17743.99225    0.01775 0.5000
  16:  23  0 23 22  0 22                 16458.71000  16458.67983    0.03017    0.10000   0.00000
16458.67983    0.03017 0.5000
  17:  23  1 23 22  0 22                 16458.71000  16458.67983    0.03017    0.10000   0.00000
16458.67983    0.03017 0.5000
  18:  23  2 21 22  2 20                 17778.57000  17778.61370   -0.04370    0.10000   0.00000
17778.61395   -0.04395 0.5000
  19:  23  3 21 22  2 20                 17778.57000  17778.61420   -0.04420    0.10000   0.00000
17778.61395   -0.04395 0.5000

NORMALIZED DIAGONAL:
   1  1.00000E+000    2  1.47065E-001    3  7.76457E-002    4  8.24537E-003    5  6.46130E-001
6  1.85927E-004
   7  9.99533E-001    8  6.95583E-002
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A          954.198( 82)           0.000
   2        20000          B          531.648(213)           0.000
```

```
  3        30000        C        351.0172(215)          0.0000
  4          200   -DeltaJ          3.90( 96)E-03       -0.00E-03
  5         2000    -DeltaK         0.0234( 45)         -0.0000
  6         1100   -DeltaJK        -0.0276( 54)          0.0000
  7        40100    -deltaJ         -3.69( 50)E-03        0.00E-03
  8        41000    -deltaK         0.0224( 42)         -0.0000
MICROWAVE AVG =      -0.000007 MHz, IR AVG =       0.00000
MICROWAVE RMS =       0.052819 MHz, IR RMS =       0.00000
```

SPFIT Details for wttt with HDO

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  6  0  5  5  1             11176.20000   11176.19350    0.00650    0.10000   0.09923
11176.18798    0.01202 0.5000
   2:   6  6  1  5  5  1             11176.20000   11176.18247    0.01753    0.10000   0.09923
11176.18798    0.01202 0.5000
   3:   8  5  4  7  4  4             11940.13000   11940.14056   -0.01056    0.10000   0.09116
   4:   9  8  2  8  7  2             15978.30000   15978.32409   -0.02409    0.10000   0.08641
   5:   9  9  1  8  8  1             17027.29000   17027.27476    0.01524    0.10000   0.09484
   6:  14  0 14 13  0 13              10242.49000   10242.51905   -0.02905    0.10000   0.07360
10242.52149   -0.03149 0.5000
   7:  14  1 14 13  0 13              10242.49000   10242.52392   -0.03392    0.10000   0.07360
10242.52149   -0.03149 0.5000
   8:  14  4 11 13  4 10              12216.53000   12216.57718   -0.04718    0.10000   0.09634
   9:  17  0 17 16  0 16              12366.11000   12366.24231   -0.13231    0.10000   0.06094
12366.24241   -0.13241 0.5000
  10:  17  1 17 16  0 16              12366.11000   12366.24251   -0.13251    0.10000   0.06094
12366.24241   -0.13241 0.5000
  11:  18  2 16 17  2 15              14401.99000   14401.76069    0.22931    0.10000   0.06064
  12:  21  0 21 20  0 20              15197.87000   15197.74646    0.12354    0.10000   0.09012
15197.74646    0.12354 0.5000
  13:  21  1 21 20  0 20              15197.87000   15197.74646    0.12354    0.10000   0.09012
15197.74646    0.12354 0.5000
  14:  21  1 20 20  1 19              15858.02000   15857.99833    0.02167    0.10000   0.06014
15857.99847    0.02153 0.5000
  15:  21  2 20 20  1 19              15858.02000   15857.99861    0.02139    0.10000   0.06014
15857.99847    0.02153 0.5000
  16:  22  1 21 21  1 20              16565.47000   16565.54975   -0.07975    0.10000   0.06676
16565.54980   -0.07980 0.5000
  17:  22  2 21 21  1 20              16565.47000   16565.54985   -0.07985    0.10000   0.06676
16565.54980   -0.07980 0.5000
  18:  22  2 20 21  2 19              17229.02000   17229.10722   -0.08722    0.10000   0.08424
17229.10973   -0.08973 0.5000
  19:  22  3 20 21  2 19              17229.02000   17229.11224   -0.09224    0.10000   0.08424
17229.10973   -0.08973 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  5.88486E-001    3  1.98502E-001    4  1.20337E-002    5  5.08682E-001
6  4.01691E-003
   7  8.81088E-002    8  9.99012E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                        NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000        A        975.1596(178)         -0.0000
   2        20000        B         529.494( 66)         -0.000
   3        30000        C        354.0067( 54)          0.0000
```

```
  4        200    -DeltaJ          0.625(110)E-03        0.000E-03
  5       2000    -DeltaK        0.010510(295)        -0.000000
  6       1100    -DeltaJK        -0.01112( 33)          0.00000
  7      40100    -deltaJ          -0.075( 84)E-03        0.000E-03
  8      41000    -deltaK           9.306(298)E-03       -0.000E-03
MICROWAVE AVG =       -0.001135 MHz, IR AVG =        0.00000
MICROWAVE RMS =        0.093339 MHz, IR RMS =        0.00000
```

SPFIT Details for wg1tw

```
                          EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  4  4  1  3  3  1             10938.25000  10938.25243  -0.00243    0.10000   0.00000
   2:  5  4  2  4  3  2             12395.46000  12395.45951   0.00049    0.10000   0.00000
   3:  6  6  0  5  5  1             16779.55000  16779.55647  -0.00647    0.10000   0.00000
16779.54792    0.00208 0.5000
   4:  6  6  1  5  5  1             16779.55000  16779.53936   0.01064    0.10000   0.00000
16779.54792    0.00208 0.5000
   5:  7  6  2  6  5  2             18221.87000  18221.87177  -0.00177    0.10000   0.00000
   6:  9  2  8  8  1  7             12043.14000  12043.12797   0.01203    0.10000   0.00000
   7:  11  0 11 10  0 10              13370.35000  13370.29918   0.05082    0.10000   0.00000
   8:  11  1 11 10  0 10              13370.37000  13370.43452  -0.06452    0.10000   0.00000
   9:  14  0 14 13  0 13              16883.85000  16883.84384   0.00616    0.10000   0.00000
  10:  14  1 13 13  1 12               17818.56000  17818.39988   0.16012    0.10000   0.00000
  11:  14  1 14 13  0 13               16883.85000  16883.84865   0.00135    0.10000   0.00000
  12:  14  2 13 13  1 12               17818.56000  17818.72408  -0.16408    0.10000   0.00000
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  3.21007E-001   3  2.07692E-001   4  1.28770E-002   5  5.34714E-001
6  6.97514E-004
   7  1.17205E-001   8  9.99986E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                     NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A         1458.781( 42)          -0.000
   2        20000          B          832.488(242)           0.000
   3        30000          C         587.0201(174)          -0.0000
   4          200    -DeltaJ          -0.03030(211)          -0.00000
   5         2000    -DeltaK            -0.0570( 49)          -0.0000
   6         1100   -DeltaJK            0.0884( 70)           0.0000
   7        40100     -deltaJ             -6.17(123)E-03         -0.00E-03
   8        41000     -deltaK              -9.90(133)E-03         0.00E-03
 MICROWAVE AVG =       0.000023 MHz, IR AVG =        0.00000
 MICROWAVE RMS =       0.073549 MHz, IR RMS =        0.00000
```

SPFIT Details for wg1tw with HDO and H2O

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  3  4  5  2  4             12760.29000   12760.28684    0.00316    0.10000   0.00000
   2:   6  3  4  5  2  4             12760.29000   12760.28684    0.00316    0.10000   0.00000
   3:   7  5  3  6  4  3             16645.30000   16645.31532   -0.01532    0.10000   0.00000
   4:   8  2  6  7  1  6             15618.40000   15618.39005    0.00995    0.10000   0.00000
   5:  10  2  9  9  2  8              13059.02000   13059.10697   -0.08697    0.10000   0.00000
   6:  10  4  7  9  4  6              14434.14000   14434.13628    0.00372    0.10000   0.00000
   7:  11  2  9 10  2  8               15278.29000   15278.20182    0.08818    0.10000   0.00000
   8:  11  3  8 10  3  7               16454.69000   16454.69988   -0.00988    0.10000   0.00000
   9:  13  0 13 12  0 12                15645.39000   15645.36816    0.02184    0.10000   0.00000
  10:  13  1 13 12  0 12                15645.40000   15645.38034    0.01966    0.10000   0.00000
  11:  14  1 13 13  1 12                17737.12000   17737.16110   -0.04110    0.10000   0.00000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  3.11662E-001    3  2.30822E-001    4  7.12813E-002    5  9.54985E-001
6  5.15537E-003
   7  9.98405E-001    8  5.85250E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                       NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A        1456.4213(310)         -0.0000
   2        20000         B         826.5009(111)          0.0000
   3        30000         C         583.8551(108)         -0.0000
   4          200    -DeltaJ         -0.01406( 40)         0.00000
   5         2000     -DeltaK          -0.14363( 86)         0.00000
   6         1100    -DeltaJK         0.15670(125)         -0.00000
   7        40100     -deltaJ           -0.934(225)E-03       -0.000E-03
   8        41000     -deltaK          -0.12176( 67)          0.00000
 MICROWAVE AVG =       -0.000326 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.040851 MHz, IR RMS =        0.00000
```

SPFIT Details for wttw

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   5  5  0  4  4  0              12493.57000   12493.71234   -0.14234    0.10000   0.00000
   2:   6  2  4  5  1  4              12156.22000   12156.19065    0.02935    0.10000   0.00000
   3:   7  7  0  6  6  1              17719.83000   17719.72152    0.10848    0.10000   0.00000
   4:  10  0 10  9  0  9               11568.04000   11567.89253    0.14747    0.10000   0.00000
11567.89499    0.14501 0.5000
   5:  10  1 10  9  0  9               11568.04000   11567.89745    0.14255    0.10000   0.00000
11567.89499    0.14501 0.5000
   6:  12  0 12 11  0 11                13779.45000   13779.44074    0.00926    0.10000   0.00000
13779.44086    0.00914 0.5000
   7:  12  1 12 11  0 11                13779.45000   13779.44098    0.00902    0.10000   0.00000
13779.44086    0.00914 0.5000
   8:  13  2 11 12  2 10                16931.38000   16931.41502   -0.03502    0.10000   0.00000
   9:  14  2 12 13  2 11                18035.22000   18035.28052   -0.06052    0.10000   0.00000
18035.31488   -0.09488 0.5000
  10:  14  3 12 13  2 11                 18035.22000   18035.34924   -0.12924    0.10000   0.00000
18035.31488   -0.09488 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  9.45806E-001    3  9.90494E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A        1305.2633( 64)         -0.0000
   2        20000         B         897.6755( 77)          0.0000
   3        30000         C        552.91483(244)         -0.00000
 MICROWAVE AVG =         0.002821 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.095790 MHz, IR RMS =        0.00000
```

SPFIT Details for wttw with HDO and H2O

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  5  4  1  4  3  1              11242.68000   11242.69479   -0.01479    0.10000   0.00000
   2:  5  4  1  4  3  1              11242.68000   11242.69479   -0.01479    0.10000   0.00000
   3:  6  4  2  5  3  2              12596.10000   12596.06054    0.03946    0.10000   0.00000
   4:  7  2  5  6  1  5              14362.91000   14362.91037   -0.00037    0.10000   0.00000
   5:  7  7  0  6  6  1              17648.78000   17648.81918   -0.03918    0.10000   0.00000
17648.77792    0.00208 0.5000
   6:  7  7  1  6  6  1              17648.78000   17648.73667    0.04333    0.10000   0.00000
17648.77792    0.00208 0.5000
   7:  8  5  4  7  4  4              17146.63000   17146.63995   -0.00995    0.10000   0.00000
   8:  11  0 11  10  0 10              12614.15000   12614.15334   -0.00334    0.10000   0.00000
12614.15390   -0.00390 0.5000
   9:  11  1 11 10  0 10              12614.15000   12614.15446   -0.00446    0.10000   0.00000
12614.15390   -0.00390 0.5000
  10:  12  5  8 11  5  7              17723.40000   17723.40041   -0.00041    0.10000   0.00000
  11:  14  1 13 13  1 12              16931.83000   16931.82833    0.00167    0.10000   0.00000
16931.82900    0.00100 0.5000
  12:  14  2 13 13  1 12              16931.83000   16931.82968    0.00032    0.10000   0.00000
16931.82900    0.00100 0.5000
  13:  15  0 15 14  0 14              17022.67000   17022.66915    0.00085    0.10000   0.00000
17022.66915    0.00085 0.5000
  14:  15  1 15 14  0 14              17022.67000   17022.66915    0.00085    0.10000   0.00000
17022.66915    0.00085 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  8.05358E-001    3  2.00194E-001    4  6.54921E-002    5  7.11906E-001
6  1.12255E-002
   7  3.35756E-001    8  9.98960E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
  1       10000         A       1300.3416(191)          0.0000
  2       20000         B        892.5002(140)         -0.0000
  3       30000         C        550.1164(111)          0.0000
  4         200    -DeltaJ           -2.430(116)E-03       -0.000E-03
  5        2000    -DeltaK            -5.25( 46)E-03        0.00E-03
  6        1100    -DeltaJK           6.57( 53)E-03       -0.00E-03
  7       40100     -deltaJ          -2.653( 84)E-03        0.000E-03
  8       41000     -deltaK           3.42( 41)E-03        0.00E-03
 MICROWAVE AVG =       -0.000083 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.014544 MHz, IR RMS =        0.00000
```

SPFIT Details for wttw with d2o

```
                              EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  5  4  1  4  3  1             10636.45000   10636.45612   -0.00612    0.10000   0.06874
   2:  5  4  1  4  3  1             10636.45000   10636.45612   -0.00612    0.10000   0.06874
   3:  6  4  3  5  3  3             12485.52000   12485.53485   -0.01485    0.10000   0.09208
   4:  6  5  1  5  4  2             13253.92000   13253.88702    0.03298    0.10000   0.04823
   5:  7  6  2  6  5  2             15624.54000   15624.54799   -0.00799    0.10000   0.09627
  6:  7  7  0  6  6  1             16582.38000   16582.48266   -0.10266    0.10000   0.09979
16582.38185   -0.00185 0.5000
  7:  7  7  1  6  6  1             16582.38000   16582.28104    0.09896    0.10000   0.09979
16582.38185   -0.00185 0.5000
  8:  8  5  4  7  4  4             16419.63000   16419.62936    0.00064    0.10000   0.09993
  9:  9  1  8  8  1  7             11043.96000   11043.95278   0.00722   0.10000   0.07853
  10:  10  1 10  9  0  9              11121.08000   11121.08584   -0.00584    0.10000   0.07249
  11:  13  0 13 12  0 12              14306.17000   14306.16820    0.00180    0.10000   0.09630
14306.16820    0.00180 0.5000
  12:  13  1 13 12  0 12              14306.17000   14306.16820    0.00180    0.10000   0.09630
14306.16820    0.00180 0.5000
  13:  14  2 12 13  2 11              17335.28000   17335.27717    0.00283    0.10000   0.09918
17335.28099   -0.00099 0.5000
  14:  14  3 12 13  2 11              17335.28000   17335.28482   -0.00482    0.10000   0.09918
17335.28099   -0.00099 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  2.86015E-001    3  2.60851E-001    4  5.97365E-002    5  9.97031E-001
6  5.26630E-003
   7  6.88389E-001    8  5.55440E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                         NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1         10000          A        1220.9315(273)          -0.0000
   2         20000          B          880.320( 50)           0.000
   3         30000          C        531.7673( 99)         -0.0000
   4           200     -DeltaJ           -3.59( 33)E-03          0.00E-03
   5          2000     -DeltaK          -0.03493(124)          0.00000
   6          1100    -DeltaJK         0.03948(154)         -0.00000
   7         40100      -deltaJ        -0.011605(228)        -0.000000
   8         41000      -deltaK         -0.03296(128)          0.00000
 MICROWAVE AVG =       -0.000101 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.011837 MHz, IR RMS =        0.00000
```

SPFIT Details for twww

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  3  2  1  2  1  1              12140.50000   12140.49271    0.00729    0.10000   0.00000
   2:  3  2  1  2  1  1              12140.50000   12140.49271    0.00729    0.10000   0.00000
   3:  4  1  3  3  0  3              11917.81000   11917.82102   -0.01102    0.10000   0.00000
   4:  4  3  1  3  2  1              18554.86000   18554.86683   -0.00683    0.10000   0.00000
   5:  5  0  5  4  0  4               9945.26000    9945.13833    0.12167    0.10000   0.00000
   6:  6  1  6  5  0  5              12172.21000   12172.28677   -0.07677    0.10000   0.00000
   7:  6  2  5  5  2  4              12427.05000   12427.09504   -0.04504    0.10000   0.00000
   8:  7  3  5  7  2  6              11109.76000   11109.75562    0.00438    0.10000   0.00000
   9:  9  2  8  8  2  7              18329.88000   18329.86150    0.01850    0.10000   0.00000
  10:  10  1 10  9  0  9              18929.74000   18929.56889    0.17111    0.10000   0.00000
  11:  10  0 10  9  0  9              18881.28000   18881.45275   -0.17275    0.10000   0.00000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  6.07113E-001    3  3.61698E-001    4  2.86064E-002    5  7.77550E-001
6  1.87713E-003
   7  9.99836E-001    8  2.07839E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A         3093.503( 43)          -0.000
   2        20000         B         1190.4341(255)          -0.0000
   3        30000         C          903.3326(174)           0.0000
   4          200    -DeltaJ         0.04957(253)          0.00000
   5         2000    -DeltaK          0.0720( 73)           0.0000
   6         1100    -DeltaJK        -0.1228( 97)          -0.0000
   7        40100     -deltaJ       -0.03391(106)         -0.00000
   8        41000     -deltaK         0.0574( 34)           0.0000
 MICROWAVE AVG =        0.001622 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.086595 MHz, IR RMS =        0.00000
```

SPFIT Details for twww with d2o

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   4  2  2  3  1  2              12829.54000   12829.53315    0.00685    0.10000   0.07063
   2:   4  2  2  3  1  2              12829.54000   12829.53315    0.00685    0.10000   0.07063
   3:   4  3  1  3  2  1              16704.29000   16704.29571   -0.00571    0.10000   0.09996
   4:   6  0  6  5  0  5              10960.95000   10961.06459   -0.11459    0.10000   0.08164
   5:   6  2  5  5  2  4              11660.97000   11660.99502   -0.02502    0.10000   0.09920
   6:   7  1  7  6  1  6              12493.10000   12492.94587    0.15413    0.10000   0.06298
   7:   7  1  7  6  0  6              12803.02000   12803.01513    0.00487    0.10000   0.09997
   8:   7  4  4  7  3  5              12386.18000   12386.17896    0.00104    0.10000   0.10000
   9:   9  0  9  8  0  8              15954.70000   15954.74082   -0.04082    0.10000   0.09786
  10:   9  1  8  8  1  7              17648.77000   17648.76305    0.00695    0.10000   0.09988

NORMALIZED DIAGONAL:
   1  1.00000E+000    2  9.99997E-001    3  2.61223E-001    4  8.55465E-002    5  8.98704E-001
6  2.54647E-003
   7  4.30675E-001    8  7.58815E-002
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                       NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1       10000        A       2764.333( 43)          0.000
   2       20000        B       1124.705( 40)         -0.000
   3       30000        C       843.9835(215)         -0.0000
   4         200   -DeltaJ      0.07328(269)        -0.00000
   5        2000    -DeltaK        0.2052( 82)        -0.0000
   6        1100   -DeltaJK         -0.2730(108)          0.0000
   7       40100    -deltaJ          -1.12( 97)E-03        0.00E-03
   8       41000    -deltaK        0.0447( 38)         -0.0000
 MICROWAVE AVG =       -0.000546 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.062753 MHz, IR RMS =        0.00000
```

SPFIT Details for twww with HDO and 2H2O

```
                              EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   3  3  1  2  2  1              16398.86000   16398.85982    0.00018    0.10000   0.07070
   2:   3  3  1  2  2  1              16398.86000   16398.85982    0.00018    0.10000   0.07070
   3:   4  2  2  3  1  2              13961.08000   13961.08639   -0.00639    0.10000   0.08607
   4:   4  2  3  3  1  3              15236.12000   15236.11569    0.00431    0.10000   0.09324
   5:   5  1  5  4  0  4              10509.98000   10509.97480    0.00520    0.10000   0.09304
   6:   6  3  4  5  3  3              12552.62000   12552.62253   -0.00253    0.10000   0.09161
   7:   7  2  6  6  2  5              14285.28000   14285.28410   -0.00410    0.10000   0.09289
   8:   7  3  5  6  3  4              14654.84000   14654.83554    0.00446    0.10000   0.08646
   9:   8  0  8  7  1  7              14905.65000   14905.64569    0.00431    0.10000   0.09307
  10:   8  1  8  7  1  7               15053.93000   15053.93716   -0.00716    0.10000   0.05568
  11:   9  0  9  8  0  8               16927.83000   16927.82812    0.00188    0.10000   0.09477
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  7.40245E-001    3  3.71324E-001    4  2.98228E-002    5  2.87889E-001
6  3.78048E-003
   7  1.56966E-001    8  9.99845E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                         NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A        3069.896( 63)          -0.000
   2        20000         B        1178.521( 35)           0.000
   3        30000         C        894.5971(212)           0.0000
   4          200    -DeltaJ       0.02187(223)          0.00000
   5         2000     -DeltaK           -8.6( 51)E-03           0.0E-03
   6         1100    -DeltaJK          - 0.0154( 72)          -0.0000
   7        40100     -deltaJ         -0.02172(134)          -0.00000
   8        41000     -deltaK         0.01840(278)           0.00000
 MICROWAVE AVG =        0.000033 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.004296 MHz, IR RMS =        0.00000
```

SPFIT Details for gwww

```
                           EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  6  0  6  5  1  5          12222.79000  12222.82495  -0.03495   0.10000  0.09067
   2:  8  0  8  7  0  7          16581.46000  16581.56142  -0.10142   0.10000  0.07277
   3:  8  0  8  7  1  7          16428.24000  16428.27258  -0.03258   0.10000  0.05196
   4:  8  1  7  7  1  6          18171.83000  18171.82137   0.00863   0.10000  0.09987
   5:  9  0  9  8  1  8          18462.25000  18462.11487   0.13513   0.10000  0.06162
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  5.69646E-001    3  9.43440E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A        2780.966(145)           0.000
   2        20000         B       1259.2319(256)           0.0000
   3        30000         C        990.4445( 60)          0.0000
 MICROWAVE AVG =       -0.005038 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.078617 MHz, IR RMS =        0.00000
```

SPFIT Details for gwww with d2o

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  3  3  0  2  2  0            13592.26000   13592.27343   -0.01343    0.10000   0.06514
   2:  3  3  0  2  2  0            13592.26000   13592.27343   -0.01343    0.10000   0.06514
   3:  4  3  2  3  2  2            15793.37000   15793.34079    0.02921    0.10000   0.08428
   4:  6  0  6  5  0  5            11740.14000   11740.06363    0.07637    0.10000   0.08436
   5:  6  0  6  5  1  5            11410.63000   11410.64540   -0.01540    0.10000   0.09423
   6:  6  1  5  5  1  4            13053.14000   13053.08182    0.05818    0.10000   0.09831
   7:  7  2  6  6  2  5            14451.67000   14451.89947   -0.22947    0.10000   0.06821
   8:  8  2  7  7  2  6            16410.91000   16410.68417    0.22583    0.10000   0.07523
   9:  8  1  7  7  1  6            16886.03000   16886.12373   -0.09373    0.10000   0.08267
  10:  8  3  6  7  3  5             16983.69000   16983.68912    0.00088    0.10000   0.09826
  11:  8  0  8  7  0  7             15364.52000   15364.52479   -0.00479    0.10000   0.06148
  12:  9  1  9  8  1  8             17162.50000   17162.51894   -0.01894    0.10000   0.09038

NORMALIZED DIAGONAL:
   1  1.00000E+000    2  2.70298E-001    3  2.22801E-001    4  3.31616E-002    5  7.95251E-001
6  9.77651E-004
   7  9.99998E-001    8  1.39128E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A        2513.922(214)           -0.000
   2        20000          B        1186.298( 57)           -0.000
   3        30000          C        917.0280(280)           0.0000
   4          200    -DeltaJ          0.1131( 86)          0.0000
   5         2000     -DeltaK          0.1861(175)           0.0000
   6         1100    -DeltaJK          -0.3013(261)           -0.0000
   7        40100      -deltaJ          -0.0700( 42)          -0.0000
   8        41000      -deltaK          0.1217(104)           0.0000
 MICROWAVE AVG =        0.000108 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.101443 MHz, IR RMS =        0.00000
```

SPFIT Details for gwww with HDO and 2H2O

```
                          EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  3  3  0  2  2  0           14841.22000   14841.28587   -0.06587    0.10000   0.06868
   2:  3  3  0  2  2  0           14841.22000   14841.28587   -0.06587    0.10000   0.06868
   3:  4  2  2  3  1  2           13506.13000   13505.90996    0.22004    0.10000   0.08272
   4:  4  2  3  3  1  3           14650.38000   14650.52946   -0.14946    0.10000   0.09243
   5:  4  3  1  3  2  1           17027.30000   17027.18099    0.11901    0.10000   0.09527
   6:  5  2  4  4  2  3           11139.04000   11138.90518    0.13482    0.10000   0.09389
   7:  5  1  5  4  0  4           11083.86000   11083.99994   -0.13994    0.10000   0.09340
   8:  7  3  5  6  3  4           15841.81000   15841.94014   -0.13014    0.10000   0.09432
   9:  8  1  8  7  1  7           16445.31000   16445.30959    0.00041    0.10000   0.10000
  10:  8  2  7  7  2  6            17551.87000   17551.79872    0.07128    0.10000   0.09833
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  6.78450E-001    3  3.51016E-001    4  3.43171E-002    5  5.68001E-001
6  6.04884E-003
   7  1.91890E-001    8  9.99324E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A        2747.692( 59)           0.000
   2        20000         B        1256.4492(258)         -0.0000
   3        30000         C        986.3222(208)          -0.0000
   4          200    -DeltaJ       0.04515(208)        -0.00000
   5         2000    -DeltaK         0.0453( 54)        -0.0000
   6         1100   -DeltaJK        -0.0921( 72)           0.0000
   7        40100     -deltaJ       -0.03020(118)          0.00000
   8        41000     -deltaK        0.04162(295)         -0.00000
 MICROWAVE AVG =       -0.000573 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.123844 MHz, IR RMS =        0.00000
```

Section 3: Kraitchman Analysis from singly deuterated isotopologues and O-O distance from calculated structures.

In this section, Kraitchman anaylsis results from the KRA fitting program are included for every tetramer conformer including at least one water. In each of these conformers, the same water molecule (in regards to relative position around the ring) was substituted with HDO with deuterium in the plane of hydrogen bonding. The results of KRA fitting show the change in position for this deuterium.

In addition, calculated O-O distance is presented in table form for each conformer. These calculated distances show an increase in O-O distance upon inclusion of water into the pure ethanol tetramers, illustrating the strength of the hydrogen bond in pure ethanol tetramers.

Table of Calculated H position vs. Kraitchman fit of H position. ** indicates high error in fit, so value not reported.

Conformer	X	Y	Z	Distance to Center of Mass	Calc. X	Calc. Y	Calc. Z	Calc. Distance to Center of Mass
wg1g2t	-0.070527	-2.127519	0.455759	2.176930734	**	1.75477	0.85915	1.953805639
wttt	0.95024	-1.917036	-0.057843	2.140403909	1.18066	2.24931	**	2.540345156
wg1tw	2.457927	-0.633641	0.278126	2.553480003	2.09037	0.54486	0.17909	2.167623672
wttw	-1.637834	1.281045	-0.203628	2.089268022	1.74118	1.29479	0.29507	2.189807124
twww	2.055524	-1.168428	0.068512	2.365395696	2.05793	1.12638	0.2348	2.357740195
gwww	0.397353	-1.464177	-0.361862	1.559694778	0.83698	1.47857	0.63819	1.814935603

Table of Calculated O-O distances, showing trend in increasing O-O distance with inclusion of water

Pure Tetramer	O-O distance	Average
2g-g+t	2.70762	2.71277
	2.71584	
	2.71993	
	2.70769	

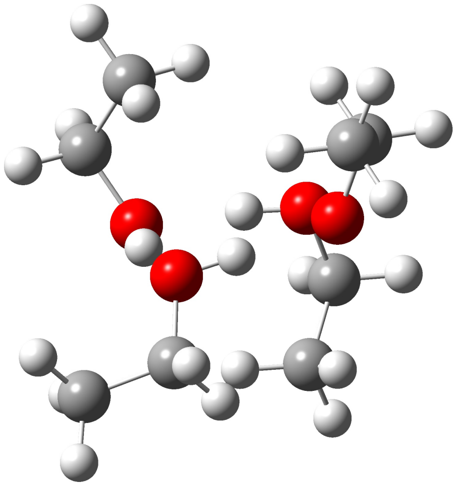
2g-2g+	2.71754	2.717545
	2.71755	
	2.71754	
	2.71755	
2tg+g-	2.69939	2.7092
	2.70873	
	2.72013	
	2.70855	

Mixed Tetramers	O-O distance	Average
wg1g2t	2.73792	2.7522
	2.75396	
	2.75617	
	2.76075	
wttt	2.76929	2.750365
	2.74803	
	2.75897	
	2.72517	
wg1g2w	2.76762	2.749715
	2.75544	
	2.72465	
	2.75115	
wttw	2.75328	2.74954
	2.76111	
	2.75985	
	2.72392	
gwww	2.74019	2.7492125

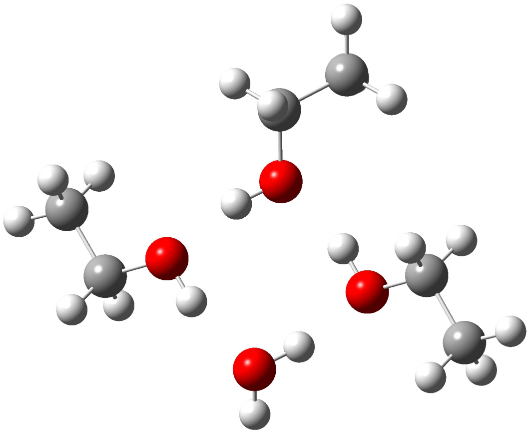
	2.7329	
	2.76598	
	2.75778	
twww	2.72331	2.740305
	2.73695	
	2.74218	
	2.75878	

Section 4: Enlarged Images of Fitted Conformers

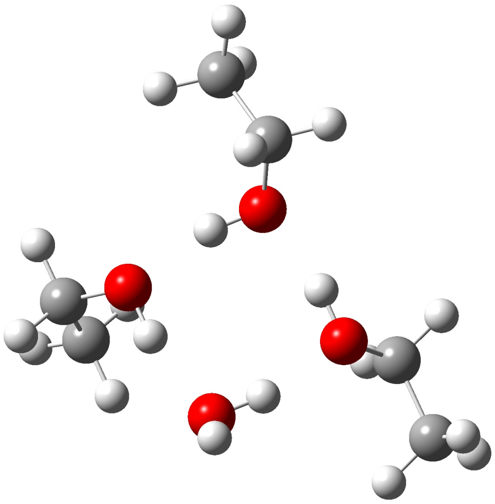
Here, enlarged images of each fitted conformer are included for reference, and to illustrate the relative geometry of ethyl groups distinguishing conformers from each other. *Ab initio* geometries are available upon request.



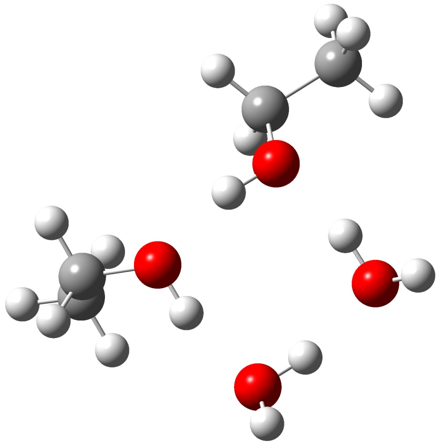
2tg+g-



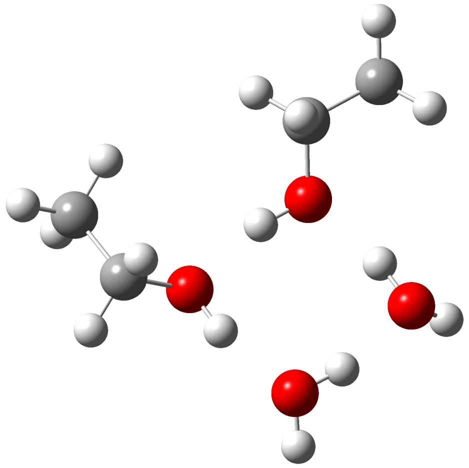
Wttt



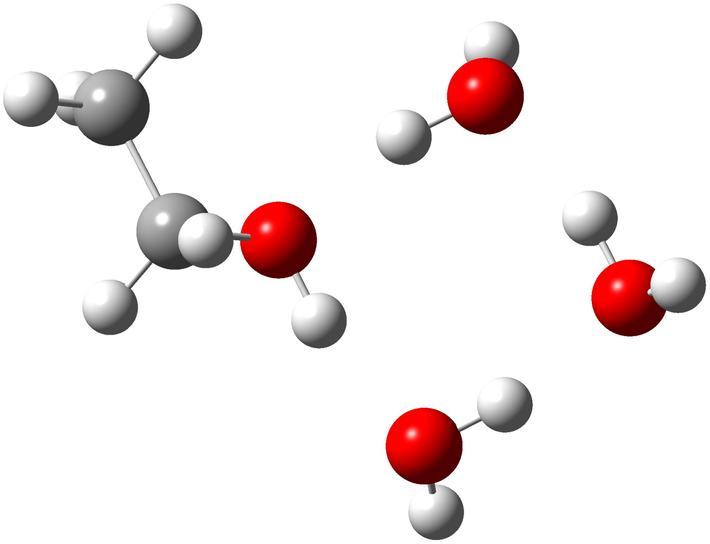
Wg1g2t



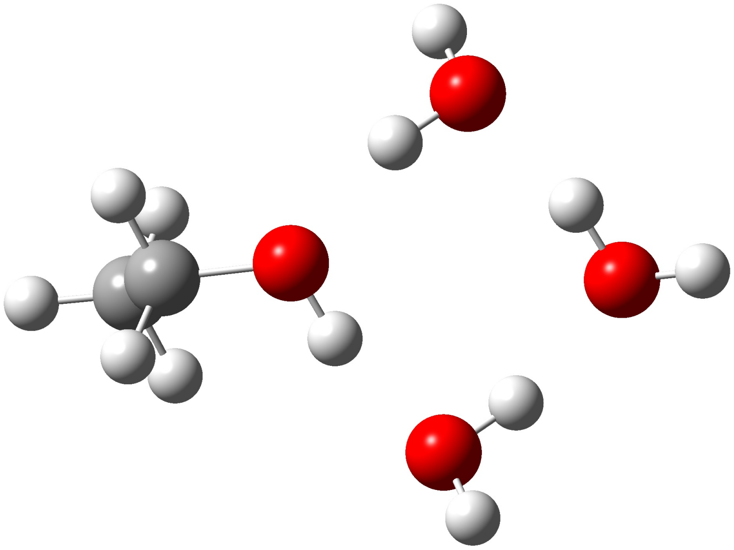
Wg1tw



Wttw



Twww



Gwww

Section 5: XIAM Results

Finally, samples from the XIAM results are included to demonstrate the calculated magnitude of splitting due to the methyl group rotation. This magnitude of splitting is lower than can be resolved with the current instrumentation, but is large enough, especially for high J states, that it may increase the error in line assignment (and thus SPFIT results) commensurately.

Sample lines fit for the 2tg+g- conformer:

```
   J K- K+  J K- K+    Sym   calc/GHz  diff/MHz     obs/GHz
 1: 10 10  1  9  9  0   S 0  10.9611722    7.5578  10.9687300   Err  .1D+01      I   .702 rigid-rigid
 2: 11  0 11 10  0 10   S 0  10.2946610   -6.1310  10.2885300   Err  .1D+01      I  2.002 rigid-rigid
 3: 12  0 12 11  0 11   S 0  11.2234430    8.0570  11.2315000   Err  .1D+01      I  1.752 rigid-rigid
```

XIAM predicted splitting for a few sample lines, illustrating a magnitude of splitting too small to resolve with the current instrumentation.

```
10 10  1   9  9  1   S 1  V 1   10.961579   .2167   .0000  19.0000   .0000   .0512  B 1  K -1 -1  t
20 18
10 10  1   9  9  1   S 2  V 1   10.961568   .3274   .0000  19.0000   .0000   .0512  B 1  K -1 -1  t
20 18


12  0 12  11  0 11   S 1  V 1   11.223443  1.0996   .0000  23.0000   .0000   .0524  B 1  K 12 11
t  1  1
12  0 12  11  0 11   S 2  V 1   11.223439  3.0994   .0000  23.0000   .0000   .0524  B 1  K 12 11
t  1  1


12 12  0  11 11  0   S 1  V 1   13.161160   .2610   .0000  23.0000   .0000   .0612  B 1  K  0  0  t
25 23
12 12  0  11 11  0   S 2  V 1   13.161179  1.0124   .0000  23.0000   .0000   .0612  B 1  K  0  0  t
25 23
```

Appendix C

SUPPLEMENTARY INFORMATION FOR CHAPTER 4

SPFIT output is included for every fitted pentamer conformer. The first 22 fits are normal isotopologues, the next 22 fits are for perdeuterated methanol and normal water clusters, the following 19 fits are perdeuterated water and normal methanol clusters, and the final 16 fits are normal methanol and normal water with a single HDO substitution. HDO1 implies the first water in the naming scheme is replaced with HDO. Likewise, HDO2 conveys the second water in each conformer is replaced with HDO.

uduud SPFIT Output

```
                          EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  10  6  4  9  5  4          13403.18000  13403.13732    0.04268    0.10000   0.07837
13403.18741   -0.00741 0.5000
   2:  10  7  4  9  6  4          13403.18000  13403.23750   -0.05750    0.10000   0.07837
13403.18741   -0.00741 0.5000
   3:  10  8  2  9  7  2          13374.99000  13374.93520    0.05480    0.10000   0.07572
   4:  10  9  2  9  8  2          13413.47000  13413.65162   -0.18162    0.10000   0.05845
   5:  12  5  7 11  5  6          12580.57000  12580.51445    0.05555    0.10000   0.09699
12580.51443    0.05557 0.5000
   6:  12  6  7 11  6  6          12580.57000  12580.51441    0.05559    0.10000   0.09699
12580.51443    0.05557 0.5000
   7:  12 10  3 11  9  3          16081.79000  16081.72266    0.06734    0.10000   0.09134
   8:  12 12  1 11 11  1          16164.42000  16164.26368    0.15632    0.10000   0.06168
   9:  13 10  3 12 10  2          16201.69000  16201.67737    0.01263    0.10000   0.09695
  10:  13 13  1 12 12  1          17513.34000  17513.43614   -0.09614    0.10000   0.08508
  11:  14 10  5 13 10  4          16344.68000  16344.73550   -0.05550    0.10000   0.09527
  12:  15  0 15 14  0 14          12286.91000  12286.96343   -0.05343    0.10000   0.09170
12286.96343   -0.05343 0.5000
  13:  15  1 15 14  1 14          12286.91000  12286.96343   -0.05343    0.10000   0.09170
12286.96343   -0.05343 0.5000
  14:  16  0 16 15  0 15          13087.50000  13087.45902    0.04098    0.10000   0.09530
13087.45902    0.04098 0.5000
  15:  16  1 16 15  1 15          13087.50000  13087.45902    0.04098    0.10000   0.09530
13087.45902    0.04098 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  9.10175E-001    3  1.28590E-001    4  9.29330E-002    5  9.99559E-001
6  1.52409E-002
   7  3.36350E-001    8  7.12606E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                     NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A        675.4497(184)         -0.0001
   2        20000         B        665.2676(114)          0.0000
   3        30000         C        400.7210(315)         -0.0000
   4          200    -DeltaJ          0.191( 40)E-03       0.000E-03
   5         2000    -DeltaK           2.215(269)E-03      -0.001E-03
   6         1100    -DeltaJK          -2.62( 32)E-03       0.00E-03
   7        40100    -deltaJ          0.0376(205)E-03     -0.0000E-03
```

```
  8      41000    -deltaK        0.02357(278)       -0.00001
MICROWAVE AVG =      -0.000588 MHz, IR AVG =       0.00000
MICROWAVE RMS =       0.087967 MHz, IR RMS =       0.00000
```

wduud SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   7  7  0  6  6  1              12238.79000   12238.76190    0.02810    0.10000   0.07494
   2:   8  4  5  7  3  5              12749.02000   12749.00105    0.01895    0.10000   0.06089
   3:   9  5  5  8  4  4              11686.92000   11686.77701    0.14299    0.10000   0.06508
   4:   9  5  5  8  4  5              14317.62000   14317.66708   -0.04708    0.10000   0.06544
   5:   9  6  3  8  7  2              15274.78000   15274.91704   -0.13704    0.10000   0.06149
   6:  12  0 12 11  1 11                11000.91000   11000.93814   -0.02814    0.10000   0.06658
11000.93814   -0.02814 0.5000
   7:  12  1 12 11  0 11                11000.91000   11000.93814   -0.02814    0.10000   0.06658
11000.93814   -0.02814 0.5000
   8:  13  6  7 12  7  6              16022.62000   16022.59102    0.02898    0.10000   0.09479
   9:  16  2 14 15  2 13                15988.04000   15988.04108   -0.00108    0.10000   0.09732
15988.04107   -0.00107 0.2500
  10:  16  2 14 15  3 13                15988.04000   15988.04106   -0.00106    0.10000   0.09732
15988.04107   -0.00107 0.2500
  11:  16  3 14 15  2 13                15988.04000   15988.04108   -0.00108    0.10000   0.09732
15988.04107   -0.00107 0.2500
  12:  16  3 14 15  3 13                15988.04000   15988.04107   -0.00107    0.10000   0.09732
15988.04107   -0.00107 0.2500
  13:  22  5 17 22  4 18                12445.56000   12445.54114    0.01886    0.10000   0.06117
  14:  22  6 16 22  5 17                11675.03000   11674.96239    0.06761    0.10000   0.05158
11674.96245    0.06755 0.5000
  15:  22  7 16 22  6 17                11675.03000   11674.96251    0.06749    0.10000   0.05158
11674.96245    0.06755 0.5000
  16:  23  8 15 23  7 16                10825.16000   10825.13797    0.02203    0.10000   0.06159
10825.14601    0.01399 0.5000
  17:  23  9 15 23  8 16                10825.16000   10825.15405    0.00595    0.10000   0.06159
10825.14601    0.01399 0.5000
  18:  26  8 18 26  7 19                13017.39000   13017.42730   -0.03730    0.10000   0.07976
13017.42735   -0.03735 0.5000
  19:  26  9 18 26  8 19                13017.39000   13017.42741   -0.03741    0.10000   0.07976
13017.42735   -0.03735 0.5000
  20:  28  5 23 28  4 24                16778.15000   16778.16885   -0.01885    0.10000   0.09682
16778.16885   -0.01885 0.5000
  21:  28  6 23 28  5 24                16778.15000   16778.16885   -0.01885    0.10000   0.09682
16778.16885   -0.01885 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  3.14541E-001    3  1.56729E-001    4  9.51216E-001    5  2.10034E-001
6  1.11882E-002
   7  7.48320E-001    8  9.91193E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                   NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000        A        893.4276( 65)        -0.0000
   2        20000        B        731.0326( 82)         0.0000
```

```
   3      30000        C       443.4182( 69)        0.0000
   4        200   -DeltaJ        -0.4339(296)E-03     -0.0000E-03
   5       2000    -DeltaK         0.200(128)E-03      -0.000E-03
   6       1100   -DeltaJK         0.071(152)E-03       0.000E-03
   7      40100    -deltaJ         -7.8( 98)E-06        0.0E-06
   8      41000    -deltaK         2.571(240)E-03      -0.000E-03
MICROWAVE AVG =      0.003837 MHz, IR AVG =      0.00000
MICROWAVE RMS =      0.062688 MHz, IR RMS =      0.00000
```

wuduu SPFIT Output

```
                          EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  7  7  0  6  6  0              12525.84000   12525.69583    0.14417    0.10000   0.08842
12525.90490   -0.06490 0.5000
   2:  7  7  1  6  6  1              12525.84000   12526.11397   -0.27397    0.10000   0.08842
12525.90490   -0.06490 0.5000
   3:  8  3  5  7  2  5              12113.02000   12113.04201   -0.02201    0.10000   0.08416
   4:  8  7  2  7  6  2              13712.52000   13712.35654    0.16346    0.10000   0.05307
   5:  9  7  3  8  6  3              14900.03000   14900.08727   -0.05727    0.10000   0.08833
   6:  10  3  8  9  3  7              10805.79000   10805.83668   -0.04668    0.10000   0.06465
   7:  10  6  5  9  7  3              16730.21000   16730.23356   -0.02356    0.10000   0.09276
   8:  10 10  0  9  8  1               12462.51000   12462.48146    0.02854    0.10000   0.07973
   9:  12 12  0 11 10  1                15365.97000   15365.97883   -0.00883    0.10000   0.09750
  10:  13  0 13 12  0 12                 12251.50000   12251.47709    0.02291    0.10000   0.08190
12251.47707    0.02293 0.5000
  11:  13  1 13 12  1 12                 12251.50000   12251.47706    0.02294    0.10000   0.08190
12251.47707    0.02293 0.5000
  12:  15  3 12 14  3 11                 16044.26000   16044.38043   -0.12043    0.10000   0.09766
16044.24502    0.01498 0.5000
  13:  15  4 12 14  4 11                 16044.26000   16044.10961    0.15039    0.10000   0.09766
16044.24502    0.01498 0.5000
  14:  18  0 18 17  0 17                 16834.46000   16834.46898   -0.00898    0.10000   0.09791
16834.46898   -0.00898 0.5000
  15:  18  1 18 17  1 17                 16834.46000   16834.46898   -0.00898    0.10000   0.09791
16834.46898   -0.00898 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  9.94875E-001    3  2.79759E-001    4  8.94716E-002    5  9.98954E-001
6  6.08476E-003
   7  2.79836E-001    8  7.88281E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                       NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A        917.9162(281)          -0.0000
   2        20000          B        688.9861( 89)           0.0000
   3        30000          C        458.8290( 74)           0.0000
   4          200    -DeltaJ          -0.382(172)E-03         0.000E-03
   5         2000     -DeltaK             0.30( 47)E-03          0.00E-03
   6         1100    -DeltaJK            -0.28( 64)E-03         -0.00E-03
   7        40100     -deltaJ          -0.089(104)E-03       -0.000E-03
   8        41000     -deltaK             0.39( 59)E-03          0.00E-03
 MICROWAVE AVG =       -0.000211 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.059659 MHz, IR RMS =        0.00000
```

wdudu SPFIT Output

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  6  1  5  5  1              10585.02000   10585.01488    0.00512    0.10000   0.09970
   2:   8  5  4  7  4  4              12499.04000   12499.13365   -0.09365    0.10000   0.07119
   3:   8  7  1  7  6  1              12131.26000   12131.17696    0.08304    0.10000   0.08446
   4:  10  3  8  9  2  8               15411.96000   15412.08436   -0.12436    0.10000   0.08610
   5:  11  3  8 10  2  8                16862.49000   16862.33756    0.15244    0.10000   0.08188
   6:  12 12  0 11 10  1                  15330.50000   15330.54925   -0.04925    0.10000   0.08968
   7:  13  0 13 12  0 12                  12556.47000   12556.48814   -0.01814    0.10000   0.09922
12556.48812   -0.01812 0.5000
   8:  13  1 13 12  1 12                  12556.47000   12556.48810   -0.01810    0.10000   0.09922
12556.48812   -0.01812 0.5000
   9:  13  3 10 12  3  9                 14407.77000   14407.67574    0.09426    0.10000   0.08629
  10:  13 13  0 12 11  1                  16460.40000   16460.38881    0.01119    0.10000   0.09601
  11:  14  5  9 13  5  8                16746.88000   16746.94595   -0.06595    0.10000   0.09587
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  2.48268E-001    3  1.28414E-001    4  7.58174E-002    5  9.77957E-001
6  8.94827E-003
   7  9.93875E-001    8  6.76459E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                        NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A         908.023( 47)           0.000
   2        20000          B        684.6166(261)          -0.0000
   3        30000          C         471.393( 32)          -0.000
   4          200    -DeltaJ            0.32( 32)E-03        -0.00E-03
   5         2000    -DeltaK            -0.79( 63)E-03        -0.00E-03
   6         1100    -DeltaJK           -0.15( 99)E-03         0.00E-03
   7        40100     -deltaJ          -0.374(209)E-03        0.000E-03
   8        41000     -deltaK           -0.54( 60)E-03        -0.00E-03
 MICROWAVE AVG =       -0.000529 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.083970 MHz, IR RMS =        0.00000
```

wudud SPFIT Output

```
                      EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   7  2  6  6  1  6              10818.09000   10818.03457    0.05543    0.10000   0.07587
   2:   8  3  6  7  2  6              12301.67000   12301.71687   -0.04687    0.10000   0.06523
   3:   9  7  2  8  8  0              16142.68000   16142.67760    0.00240    0.10000   0.07070
   4:   9  8  1  8  6  2              11359.56000   11359.50928    0.05072    0.10000   0.09777
   5:   9  9  1  8  8  1              16142.68000   16142.68960   -0.00960    0.10000   0.07069
   6:  10  9  1  9  8  1              14621.85000   14622.06214   -0.21214    0.10000   0.05253
   7:  11  4  7 10  3  7              16583.61000   16583.52774    0.08226    0.10000   0.09480
   8:  11 10  1 10  9  1              16221.01000   16220.91394    0.09606    0.10000   0.09234
   9:  13  0 13 12  0 12              12438.22000   12438.20824    0.01176    0.10000   0.09871
12438.20821    0.01179 0.5000
  10:  13  1 13 12  1 12              12438.22000   12438.20818    0.01182    0.10000   0.09871
12438.20821    0.01179 0.5000
  11:  14  4 10 13  4  9              15907.92000   15907.94459   -0.02459    0.10000   0.07593
  12:  14  4 11 13  4 10              15247.08000   15247.08392   -0.00392    0.10000   0.06822
  13:  19 14  6 18 13  6              17155.33000   17155.32994    0.00006    0.10000   0.10000
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  9.02122E-001   3  2.24735E-001   4  7.54415E-002   5  9.90114E-001
6  3.31107E-002
   7  1.44199E-001   8  4.42543E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1       10000         A        914.6397(207)         -0.0000
   2       20000         B        681.3030( 73)          0.0000
   3       30000         C        466.4360(174)         -0.0000
   4         200    -DeltaJ          0.413( 71)E-03        0.000E-03
   5        2000     -DeltaK         -0.901(132)E-03        0.000E-03
   6        1100    -DeltaJK          0.493(202)E-03       -0.000E-03
   7       40100     -deltaJ         -0.281( 37)E-03       -0.000E-03
   8       41000     -deltaK         -0.444(140)E-03        0.000E-03
 MICROWAVE AVG =       0.000133 MHz, IR AVG =        0.00000
 MICROWAVE RMS =       0.076211 MHz, IR RMS =        0.00000
```

wuudu SPFIT Output

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   7  1  6  6  0  6              10998.45000   10998.35513    0.09487    0.10000   0.06100
   2:   8  2  7  7  1  7              12580.57000   12580.59629   -0.02629    0.10000   0.06293
   3:   8  4  5  7  3  5              12486.20000   12486.11631    0.08369    0.10000   0.04908
   4:   9  6  4  8  5  4              14317.62000   14317.68787   -0.06787    0.10000   0.09416
   5:  10  4  6  9  4  5               12379.56000   12379.66067   -0.10067    0.10000   0.07489
   6:  10  5  5  9  5  4               12346.39000   12346.39997   -0.00997    0.10000   0.09937
   7:  11  1 10 10  1  9                11015.57000   11015.61942   -0.04942    0.10000   0.08385
11015.60634   -0.03634 0.5000
   8:  11  2 10 10  2  9                11015.57000   11015.59327   -0.02327    0.10000   0.08385
11015.60634   -0.03634 0.5000
   9:  11  3  9 10  3  8               11686.92000   11686.92307   -0.00307    0.10000   0.04733
  10:  11  4  7 10  4  6                13188.17000   13188.01047    0.15953    0.10000   0.06540
  11:  11  4  8 10  3  8                17192.21000   17192.31225   -0.10225    0.10000   0.08104
  12:  11  4  8 10  4  7                12360.68000   12360.80872   -0.12872    0.10000   0.04674
  13:  11 10  1 10  9  1                 16428.60000   16428.53919    0.06081    0.10000   0.09387
  14:  12  4  9 11  4  8                13272.75000   13272.65463    0.09537    0.10000   0.06680
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  6.42200E-001    3  2.68057E-001    4  1.63996E-001    5  9.57933E-001
6  2.76811E-002
   7  9.31477E-001    8  6.09451E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                   NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
  1       10000         A        909.4783(115)          0.0000
  2       20000         B        700.3918( 83)         -0.0000
  3       30000         C        455.0000(156)          0.0000
  4         200    -DeltaJ          0.182( 66)E-03        0.000E-03
  5        2000    -DeltaK            1.45( 37)E-03         0.00E-03
  6        1100   -DeltaJK           -0.91( 44)E-03        -0.00E-03
  7       40100     -deltaJ        -0.0190(100)E-03      -0.0000E-03
  8       41000     -deltaK           1.43( 46)E-03         0.00E-03
 MICROWAVE AVG =        0.001468 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.086883 MHz, IR RMS =        0.00000
```

wuwdu SPFIT Output

```
                     EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  5  4  2  4  3  2              10502.95000   10503.03792   -0.08792    0.10000   0.07590
   2:  6  3  4  5  2  4              11228.24000   11228.15953    0.08047    0.10000   0.07988
   3:  8  3  6  7  3  5              10252.16000   10252.13874    0.02126    0.10000   0.09759
   4:  9  1  8  8  0  8              16621.88000   16621.89036   -0.01036    0.10000   0.09945
   5:  9  8  1  8  7  1              15411.96000   15411.97334   -0.01334    0.10000   0.09950
   6:  12  9  3 12  8  5              11656.86000   11656.87289   -0.01289    0.10000   0.07395
11656.87105   -0.01105 0.5000
   7:  12  9  4 12  8  4              11656.86000   11656.86922   -0.00922    0.10000   0.07395
11656.87105   -0.01105 0.5000
   8:  15  9  7 15  6  9              11456.09000   11456.03639    0.05361    0.10000   0.09178
   9:  18  5 13 18 16  3               11087.56000   11087.57610   -0.01610    0.10000   0.08003
  10:  19 12  7 19 11  9                17155.33000   17155.33569   -0.00569    0.10000   0.09511
17155.33568   -0.00568 0.5000
  11:  19 12  8 19  9 10                17155.33000   17155.33567   -0.00567    0.10000   0.09511
17155.33568   -0.00568 0.5000
  12:  25 10 16 25  9 16                16628.15000   16628.15178   -0.00178    0.10000   0.09593
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  1.66324E-001    3  4.65624E-001    4  9.92650E-001    5  1.15464E-001
6  3.18394E-001
   7  4.26456E-002    8  7.54735E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                  NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A        1214.9415(118)          -0.0000
   2        20000          B         764.8926(140)           0.0000
   3        30000          C         521.5809(280)          -0.0000
   4          200    -DeltaJ          -0.278( 84)E-03       -0.000E-03
   5         2000    -DeltaK             2.04( 39)E-03        0.00E-03
   6         1100    -DeltaJK          0.319(117)E-03        0.000E-03
   7        40100     -deltaJ           -7.9(251)E-06         -0.0E-06
   8        41000     -deltaK          -0.299( 40)E-03       -0.000E-03
 MICROWAVE AVG =       0.000911 MHz, IR AVG =        0.00000
 MICROWAVE RMS =       0.042701 MHz, IR RMS =        0.00000
```

wuwuu SPFIT Output

```
                        EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  3  4  5  2  4              11300.96000   11300.99330   -0.03330    0.10000   0.06566
   2:   7  2  5  6  1  5              12580.57000   12580.53077    0.03923    0.10000   0.08137
   3:   7  4  3  6  3  3              15210.03000   15210.03199   -0.00199    0.10000   0.09961
   4:   7  6  1  6  5  1              12757.58000   12757.57768    0.00232    0.10000   0.08374
   5:   8  8  0  7  6  1              11368.94000   11368.92084    0.01916    0.10000   0.06462
   6:   9  2  7  8  2  6              11584.02000   11583.98912    0.03088    0.10000   0.08796
   7:   9  6  4  8  6  3              12170.29000   12170.39247   -0.10247    0.10000   0.06367
   8:  10  4  6  9  4  5              13691.22000   13691.30080   -0.08080    0.10000   0.07605
   9:  10  8  3  9  6  4              13586.82000   13586.71893    0.10107    0.10000   0.04801
  10:  11  6  6 10  6  5              14816.40000   14816.36454    0.03546    0.10000   0.09161
  11:  13  3 10 12  3  9              16537.48000   16537.49757   -0.01757    0.10000   0.09848
  12:  12  0 12 11  0 11              12890.39000   12890.38877    0.00123    0.10000   0.09994
12890.38587    0.00413 0.5000
  13:  12  1 12 11  1 11              12890.39000   12890.38298    0.00702    0.10000   0.09994
12890.38587    0.00413 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  9.97985E-001   3  3.38525E-001   4  1.92323E-001   5  7.99731E-001
6  1.98140E-002
   7  1.41440E-001   8  9.93425E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A        1201.6113(218)         -0.0000
   2        20000         B         781.5719(127)          0.0000
   3        30000         C         519.5154(130)          0.0000
   4          200    -DeltaJ          -0.457(184)E-03       -0.000E-03
   5         2000    -DeltaK            0.70( 39)E-03        -0.00E-03
   6         1100   -DeltaJK           -0.39( 58)E-03         0.00E-03
   7        40100     -deltaJ          -0.830(123)E-03       -0.000E-03
   8        41000     -deltaK            2.33( 33)E-03        0.00E-03
 MICROWAVE AVG =      -0.000323 MHz, IR AVG =        0.00000
 MICROWAVE RMS =       0.052284 MHz, IR RMS =        0.00000
```

wwdud SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  2  4  5  1  4              11205.43000   11205.54643   -0.11643    0.10000   0.05936
   2:   6  4  3  5  3  3              11520.72000   11520.60723    0.11277    0.10000   0.05814
   3:   7  2  6  6  1  6              13286.13000   13286.11138    0.01862    0.10000   0.09802
   4:   7  3  4  6  2  4              12883.95000   12883.91421    0.03579    0.10000   0.08476
   5:   7  5  2  6  4  2              13272.75000   13272.80765   -0.05765    0.10000   0.08900
   6:   8  6  2  7  5  2              10554.43000   10554.42103    0.00897    0.10000   0.09953
   7:  10  9  1  9  8  1              13403.18000   13403.18274   -0.00274    0.10000   0.09856
   8:  15  0 15 14  0 14              17597.44000   17597.43999    0.00001    0.10000   0.10000
   9:  19 12  7 19 13  7              10058.26000   10058.25902    0.00098    0.10000   0.09619
  10:  20 13  7 20 12  9              10737.50000   10737.51601   -0.01601    0.10000   0.09751
10737.50056   -0.00056 0.5000
  11:  20 13  8 20 12  8              10737.50000   10737.48512    0.01488    0.10000   0.09751
10737.50056   -0.00056 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  5.19641E-001    3  9.94831E-002    4  9.99211E-001    5  1.96533E-002
6  9.89339E-002
   7  1.46993E-001    8  7.87303E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                   NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A        1079.4438(212)         -0.0000
   2        20000         B         856.7747(116)          0.0000
   3        30000         C         573.1190(316)         -0.0000
   4          200    -DeltaJ          -0.359(112)E-03        0.000E-03
   5         2000    -DeltaK            -3.31( 41)E-03        -0.00E-03
   6         1100    -DeltaJK            5.56( 37)E-03         0.00E-03
   7        40100     -deltaJ        -0.3157(261)E-03      -0.0000E-03
   8        41000     -deltaK           -3.37( 38)E-03        -0.00E-03
 MICROWAVE AVG =       -0.000023 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.055957 MHz, IR RMS =        0.00000
```

wwuud SPFIT Output

```
                          EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  2  4  5  1  4              11294.94000   11294.95577   -0.01577    0.10000   0.07073
   2:   6  2  5  5  1  5              11603.10000   11603.23108   -0.13108    0.10000   0.05645
   3:   6  5  1  5  4  1              12457.00000   12456.94025    0.05975    0.10000   0.06514
   4:   6  5  2  5  4  1              12421.73000   12421.68784    0.04216    0.10000   0.06795
   5:   6  6  1  5  5  1              13385.09000   13385.07731    0.01269    0.10000   0.06129
   6:   8  2  7  7  1  7              15492.08000   15492.01613    0.06387    0.10000   0.09369
   7:   8  4  4  7  5  3              16328.56000   16328.71089   -0.15089    0.10000   0.05779
   8:   8  6  3  7  5  3              16267.51000   16267.43045    0.07955    0.10000   0.05833
   9:   8  6  3  7  6  2              11586.38000   11586.26784    0.11216    0.10000   0.07645
  10:   9  1  8  8  1  7               10821.86000   10821.93140   -0.07140    0.10000   0.09195
  11:   9  4  5  8  6  2               13812.51000   13812.51970   -0.00970    0.10000   0.09834
  12:  12  0 12 11  0 11                 13087.50000   13087.48183    0.01817    0.10000   0.09954
13087.48174    0.01826 0.2500
  13:  12  0 12 11  1 11                 13087.50000   13087.48162    0.01838    0.10000   0.09954
13087.48174    0.01826 0.2500
  14:  12  1 12 11  0 11                 13087.50000   13087.48187    0.01813    0.10000   0.09954
13087.48174    0.01826 0.2500
  15:  12  1 12 11  1 11                 13087.50000   13087.48166    0.01834    0.10000   0.09954
13087.48174    0.01826 0.2500
  16:  12  9  3 11  9  2                17192.21000   17192.22447   -0.01447    0.10000   0.09893
17192.22092   -0.01092 0.5000
  17:  12 11  2 11 11  1                 17192.21000   17192.21737   -0.00737    0.10000   0.09893
17192.22092   -0.01092 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  3.87916E-001    3  3.17743E-001    4  1.27550E-001    5  9.99463E-001
6  3.05012E-002
   7  9.34717E-001    8  9.89321E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A        1151.8915(224)          0.0000
   2        20000          B        844.5529(110)          -0.0000
   3        30000          C        526.6160(134)          -0.0000
   4          200    -DeltaJ           0.030(187)E-03       -0.000E-03
   5         2000    -DeltaK          -0.917(302)E-03       -0.000E-03
   6         1100    -DeltaJK           1.22( 46)E-03        0.00E-03
   7        40100     -deltaJ         -0.135(124)E-03       -0.000E-03
   8        41000     -deltaK           0.83( 40)E-03        0.00E-03
 MICROWAVE AVG =       -0.000101 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.075619 MHz, IR RMS =        0.00000
```

wuwud SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  5  5  1  4  4  1              11675.03000   11675.15247   -0.12247    0.10000   0.08298
   2:  7  2  5  6  1  5              12170.29000   12170.36266   -0.07266    0.10000   0.08096
   3:  7  3  5  6  2  5              12837.50000   12837.35968    0.14032    0.10000   0.05839
   4:  9  2  8  8  2  7              10532.44000   10532.39882    0.04118    0.10000   0.07950
   5: 10  3  8  9  3  7              12360.68000   12360.66081    0.01919    0.10000   0.05820
   6: 11  5  6 10  5  5              14458.78000   14458.92311   -0.14311    0.10000   0.07445
   7: 11 10  1 10  9  1              11645.79000   11645.71374    0.07626    0.10000   0.07344
   8: 11 10  1 10 10  0              15310.73000   15310.67850    0.05150    0.10000   0.07241
   9: 13  3 10 12  3  9              16441.28000   16441.30526   -0.02526    0.10000   0.09769
  10: 14  6  8 14  7  8              10704.66000   10704.57775    0.08225    0.10000   0.08863
  11: 16  0 16 15  0 15              16953.67000   16953.66549    0.00451    0.10000   0.09996
16953.66540    0.00460 0.2500
  12: 16  0 16 15  1 15              16953.67000   16953.66524    0.00476    0.10000   0.09996
16953.66540    0.00460 0.2500
  13: 16  1 16 15  0 15              16953.67000   16953.66557    0.00443    0.10000   0.09996
16953.66540    0.00460 0.2500
  14: 16  1 16 15  1 15              16953.67000   16953.66531    0.00469    0.10000   0.09996
16953.66540    0.00460 0.2500
  15: 16 13  3 16 12  5              16682.13000   16682.14849   -0.01849    0.10000   0.09937
16682.14849   -0.01849 0.5000
  16: 16 13  4 16 10  6              16682.13000   16682.14849   -0.01849    0.10000   0.09937
16682.14849   -0.01849 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  7.07922E-001   3  3.17020E-001   4  9.99995E-001   5  2.82065E-001
6  5.05253E-002
   7  1.74063E-001   8  8.22635E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1       10000        A       1225.2988(114)          0.0000
   2       20000        B        754.1832( 81)          0.0000
   3       30000        C        516.9673( 99)          0.0000
   4         200    -DeltaJ        -1.310( 34)E-03       -0.000E-03
   5        2000    -DeltaK        -2.590( 94)E-03       -0.000E-03
   6        1100    -DeltaJK        3.880(116)E-03        0.000E-03
   7       40100     -deltaJ       -0.0130(209)E-03      -0.0000E-03
   8       41000     -deltaK       -0.019( 39)E-03        0.000E-03
 MICROWAVE AVG =        0.002775 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.081008 MHz, IR RMS =        0.00000
```

wwduu SPFIT Output

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  6  2  4  5  1  4              11113.73000  11113.70570    0.02430    0.10000   0.09425
   2:  7  4  3  6  3  3              14862.51000  14862.56686   -0.05686    0.10000   0.07050
   3:  7  6  2  6  3  3              14856.98000  14856.90944    0.07056    0.10000   0.07064
   4:  8  3  6  7  2  6              15247.08000  15247.08628   -0.00628    0.10000   0.09801
   5:  9  4  5  8  4  4              13050.90000  13050.96842   -0.06842    0.10000   0.05418
   6:  9  5  4  8  5  3              12844.58000  12844.58935   -0.00935    0.10000   0.07804
   7:  9  5  5  8  5  4              12890.39000  12890.56966   -0.17966    0.10000   0.05136
   8:  9  6  4  8  6  3              12931.25000  12931.06785    0.18215    0.10000   0.04803
   9:  10  0 10  9  0  9              11100.96000  11100.82974    0.13026    0.10000   0.08479
11100.82468    0.13532 0.2500
  10:  10  0 10  9  1  9              11100.96000  11100.81681    0.14319    0.10000   0.08479
11100.82468    0.13532 0.2500
  11:  10  1 10  9  0  9              11100.96000  11100.83256    0.12744    0.10000   0.08479
11100.82468    0.13532 0.2500
  12:  10  1 10  9  1  9              11100.96000  11100.81963    0.14037    0.10000   0.08479
11100.82468    0.13532 0.2500
  13:  10  2  8  9  3  7              12821.90000  12821.98450   -0.08450    0.10000   0.07515
  14:  11  0 11 10  0 10               12170.29000  12170.36884   -0.07884    0.10000   0.06194
12170.36743   -0.07743 0.5000
  15:  11  0 11 10  1 10               12170.29000  12170.36602   -0.07602    0.10000   0.06194
12170.36743   -0.07743 0.5000
  16:  11  1 10 10  1  9              13033.30000  13033.21247    0.08753    0.10000   0.06206
  17:  11  1 11 10  0 10               12170.29000  12170.36945   -0.07945    0.10000   0.06194
12170.36804   -0.07804 0.5000
  18:  11  1 11 10  1 10               12170.29000  12170.36663   -0.07663    0.10000   0.06194
12170.36804   -0.07804 0.5000
  19:  11  2 10 10  1  9              13033.30000  13033.26862    0.03138    0.10000   0.06203
  20:  11  4  7 10  5  6              15042.12000  15042.08543    0.03457    0.10000   0.09679
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  9.99591E-001    3  2.03988E-001    4  6.46956E-002    5  9.84547E-001
6  6.61688E-003
   7  2.10615E-001    8  7.35403E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A        1159.805( 71)          0.000
   2        20000         B        829.5533(185)         -0.0000
   3        30000         C        532.9132(241)          0.0000
   4          200    -DeltaJ            2.41( 51)E-03       -0.00E-03
   5         2000    -DeltaK             1.66( 99)E-03       -0.00E-03
   6         1100   -DeltaJK           -1.11(145)E-03        0.00E-03
   7        40100    -deltaJ           -1.57( 36)E-03        0.00E-03
   8        41000    -deltaK             1.52(116)E-03       -0.00E-03
 MICROWAVE AVG =       0.000350 MHz, IR AVG =        0.00000
```

```
MICROWAVE RMS =        0.091813 MHz, IR RMS =        0.00000
```

wwudu SPFIT Output

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  2  5  5  1  5              11343.02000   11342.54129    0.47871    0.10000   0.06430
   2:   6  3  3  5  2  3              10818.09000   10818.16126   -0.07126    0.10000   0.09936
   3:   6  4  2  5  3  2              11165.62000   11165.56121    0.05879    0.10000   0.09956
   4:   6  5  2  5  4  2              12106.44000   12106.46847   -0.02847    0.10000   0.09990
   5:   7  1  6  6  0  6              13234.95000   13235.25878   -0.30878    0.10000   0.08692
   6:   7  4  4  6  3  4              13245.56000   13245.77927   -0.21927    0.10000   0.09358
   7:   9  4  6  8  3  6              16887.46000   16887.37246    0.08754    0.10000   0.09905
   8:   9  6  4  8  5  4              17289.13000   17289.09859    0.03141    0.10000   0.09987
   9:  12  4  9 11  4  8               16196.74000   16196.74007   -0.00007    0.10000   0.10000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  1.74717E-001    3  5.51945E-001    4  1.56980E-001    5  4.48982E-002
6  8.71710E-003
   7  6.33446E-001    8  9.98371E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                         NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
  1        10000         A        1099.576( 61)          -0.000
  2        20000         B         841.749( 32)           0.000
  3        30000         C         562.905(153)           0.000
  4          200    -DeltaJ           9.39( 73)E-03        0.00E-03
  5         2000    -DeltaK        0.01710(157)          0.00000
  6         1100    -DeltaJK      -0.04156(278)         -0.00001
  7        40100     -deltaJ         -2.42( 41)E-03       -0.00E-03
  8        41000     -deltaK       0.03400(260)          0.00001
 MICROWAVE AVG =        0.003178 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.208323 MHz, IR RMS =        0.00000
```

wwuwu SPFIT Output

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   5  2  4  4  1  4              11493.78000   11493.77968    0.00032    0.10000   0.07403
   2:   7  4  4  6  3  4              17082.38000   17082.34895    0.03105    0.10000   0.07494
   3:   9  2  8  8  2  7              12665.57000   12665.52778    0.04222    0.10000   0.06691
   4:  10  1 10  9  0  9               12890.39000   12890.36405    0.02595    0.10000   0.06384
   5:  10  9  1  9  8  1              11579.51000   11579.49323    0.01677    0.10000   0.09314
   6:  11  5  7 10  5  6               16834.46000   16834.38640    0.07360    0.10000   0.06641
   7:  11 10  2 10  8  3                16792.26000   16792.43347   -0.17347    0.10000   0.04711
   8:  12  1 12 11  1 11                15356.67000   15356.68925   -0.01925    0.10000   0.09365
   9:  12  4  8 12  5  8               13333.34000   13333.32328    0.01672    0.10000   0.09341
  10:  15  6 10 14  7  8                12434.88000   12434.87407    0.00593    0.10000   0.09916
  11:  16  4 12 16  5 12                12866.27000   12866.27898   -0.00898    0.10000   0.08989
  12:  17  4 14 16  5 12                15137.97000   15137.95739    0.01261    0.10000   0.09817
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  8.13693E-001    3  2.02882E-001    4  2.06796E-001    5  9.40170E-001
6  2.27801E-002
   7  1.50284E-001    8  4.58860E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A       1663.8654(136)          -0.0000
   2        20000          B        879.0923( 74)           0.0000
   3        30000          C        618.6094(107)          -0.0000
   4          200    -DeltaJ          -1.774( 70)E-03       -0.000E-03
   5         2000    -DeltaK          -6.190(180)E-03       -0.000E-03
   6         1100    -DeltaJK          5.766(248)E-03        0.000E-03
   7        40100     -deltaJ          0.449( 38)E-03       -0.000E-03
   8        41000     -deltaK         -1.058(115)E-03        0.000E-03
 MICROWAVE AVG =        0.001956 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.057831 MHz, IR RMS =        0.00000
```

wwdwd SPFIT Output

```
                        EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   7  2  5  6  5  1              16537.48000   16537.59496   -0.11496    0.10000   0.07095
   2:   8  5  3  8  6  3              11062.45000   11062.33661    0.11339    0.10000   0.05281
   3:   8  6  2  8  7  2              12815.64000   12815.66617   -0.02617    0.10000   0.07869
12815.65812   -0.01812 0.5000
   4:   8  8  1  8  5  3              12815.64000   12815.65006   -0.01006    0.10000   0.07869
12815.65812   -0.01812 0.5000
   5:   9  5  5  9  4  5              11000.91000   11000.91351   -0.00351    0.10000   0.05042
   6:  10  1 10  9  1  9               13139.50000   13139.42921    0.07079    0.10000   0.08094
   7:  10  2  9  9  2  8              14161.38000   14161.34682    0.03318    0.10000   0.06936
   8:  11  5  6 10  5  5               17192.21000   17192.13739    0.07261    0.10000   0.08646
   9:  12  1 11 11  1 10                16700.90000   16700.96638   -0.06638    0.10000   0.08191
  10:  12  4  8 12  5  8                12573.30000   12573.34172   -0.04172    0.10000   0.06302
  11:  14  3 12 13 12  2                 10480.21000   10480.22694   -0.01694    0.10000   0.09605
  12:  16 12  4 16 11  6                 13196.84000   13196.85535   -0.01535    0.10000   0.09917
  13:  17  4 13 17  5 13                 12113.02000   12112.96460    0.05540    0.10000   0.07682
  14:  21 18  3 21 17  5                 15058.29000   15058.31579   -0.02579    0.10000   0.09468
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  9.14076E-001    3  1.29434E-001    4  9.99747E-001    5  6.25221E-002
6  1.78570E-002
   7  2.48723E-001    8  5.86764E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                     NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A        1630.1266(144)           0.0000
   2        20000          B         895.6917(175)           0.0000
   3        30000          C         631.7337(192)          -0.0000
   4          200    -DeltaJ           -1.416( 90)E-03       -0.000E-03
   5         2000    -DeltaK           -3.219(168)E-03       -0.000E-03
   6         1100    -DeltaJK           2.062(263)E-03        0.000E-03
   7        40100     -deltaJ           0.257( 34)E-03        0.000E-03
   8        41000     -deltaK          -0.671(115)E-03       -0.000E-03
 MICROWAVE AVG =        0.003276 MHz, IR AVG =         0.00000
 MICROWAVE RMS =        0.060891 MHz, IR RMS =         0.00000
```

wwuwd SPFIT Output

```
                  EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  8  5  3  8  4  5             12804.99000   12805.06233   -0.07233    0.10000   0.06851
   2:  8  6  2  8  7  2             14816.40000   14816.43668   -0.03668    0.10000   0.06608
14816.43250   -0.03250 0.2000
   3:  8  8  1  8  5  3             14816.40000   14816.43146   -0.03146    0.10000   0.06608
14816.43250   -0.03250 0.8000
   4:  9  1  8  8  1  7             12737.52000   12737.51465    0.00535    0.10000   0.06142
   5:  9  1  9  8  0  8             11579.51000   11579.50925    0.00075    0.10000   0.04744
   6:  10  1 10  9  0  9             12799.09000   12798.96912    0.12088    0.10000   0.06951
   7:  10  3  7  9  3  6             15274.78000   15274.76750    0.01250    0.10000   0.06455
   8:  11  2 10 10  2  9              15082.33000   15082.34437   -0.01437    0.10000   0.04561
   9:  11  7  4 11  6  6              16731.27000   16731.24684    0.02316    0.10000   0.06733
16731.23381    0.03619 0.5000
  10:  11  7  5 11  4  7              16731.27000   16731.22078    0.04922    0.10000   0.06733
16731.23381    0.03619 0.5000
  11:  13  5  8 13  6  8              16621.88000   16621.84974    0.03026    0.10000   0.07510
  12:  13 13  0 12 12  0               10625.00000   10625.15190   -0.15190    0.10000   0.07381
  13:  15  3 12 15  4 12               12301.67000   12301.71641   -0.04641    0.10000   0.05727
  14:  15 11  4 15 10  6               14488.45000   14488.37342    0.07658    0.10000   0.09288
  15:  17  3 14 16  4 12               12368.74000   12368.69624    0.04376    0.10000   0.09767
  16:  17  3 14 17  4 14               12684.51000   12684.58206   -0.07206    0.10000   0.08256
  17:  25 20  6 25 21  4               15137.97000   15137.96015    0.00985    0.10000   0.09976
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  1.75705E-001    3  9.87771E-001    4  8.84008E-001    5  8.05712E-002
6  1.87466E-002
   7  4.37870E-001    8  5.90973E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
              NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A        1737.4850(148)          -0.0000
   2        20000          B         866.9146( 56)          -0.0000
   3        30000          C         613.2547( 73)          -0.0000
   4          200     -DeltaJ          -0.813( 57)E-03        0.000E-03
   5         2000     -DeltaK          -1.710(146)E-03        0.000E-03
   6         1100    -DeltaJK           0.997(166)E-03       -0.000E-03
   7        40100     -deltaJ          0.2717(251)E-03     -0.0000E-03
   8        41000     -deltaK          -0.485( 60)E-03        0.000E-03
 MICROWAVE AVG =       -0.003563 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.064195 MHz, IR RMS =        0.00000
```

wwwdd SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  7  4  4  6  4  3              12931.25000   12931.24752    0.00248    0.10000   0.09999
   2:  8  7  1  7  7  0              16164.42000   16164.42307   -0.00307    0.10000   0.09999
   3:  10  1  9  9  1  8              14523.34000   14523.33973    0.00027    0.10000   0.07071
   4:  10  1  9 10  1 10               10909.20000   10909.32869   -0.12869    0.10000   0.07861
   5:  10  2  9  9  2  8              14523.34000   14523.33955    0.00045    0.10000   0.07071
   6:  13  3 10 13  3 11                12026.68000   12026.52980    0.15020    0.10000   0.06927
12026.52983    0.15017 0.6667
   7:  13  4 10 13  2 11                12026.68000   12026.52991    0.15009    0.10000   0.06927
12026.52983    0.15017 0.3333
   8:  17  3 14 17  3 15                16628.15000   16628.15868   -0.00868    0.10000   0.09992
16628.15868   -0.00868 0.5000
   9:  17  4 14 17  2 15                16628.15000   16628.15868   -0.00868    0.10000   0.09992
16628.15868   -0.00868 0.5000
  10:  20  7 13 20  7 14                15376.74000   15376.73865    0.00135    0.10000   0.09993
15376.73870    0.00130 0.5000
  11:  20  8 13 20  6 14                15376.74000   15376.73875    0.00125    0.10000   0.09993
15376.73870    0.00130 0.5000
  12:  22 11 11 22 11 12                  12844.58000   12844.63341   -0.05341    0.10000   0.09669
  13:  22 13 10 22 11 11                  11566.97000   11566.93409    0.03591    0.10000   0.09850
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  5.93398E-001    3  9.89076E-002    4  9.99938E-001    5  2.62638E-001
6  4.22835E-003
   7  2.21624E-001    8  9.53733E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                         NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A        1289.219( 44)          -0.000
   2        20000          B       1148.9067(149)           0.0000
   3        30000          C        640.0460(175)          -0.0000
   4          200    -DeltaJ           -3.111(289)E-03        0.000E-03
   5         2000    -DeltaK             -7.02( 80)E-03        0.00E-03
   6         1100   -DeltaJK              9.51(104)E-03       -0.00E-03
   7        40100    -deltaJ            0.980(137)E-03       -0.000E-03
   8        41000    -deltaK         -0.01680(244)          0.00000
 MICROWAVE AVG =       -0.000327 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.065838 MHz, IR RMS =        0.00000
```

wwdwu SPFIT Output

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  4  4  0  3  3  0             12844.58000  12844.69507  -0.11507    0.10000   0.08937
   2:  8  1  7  7  1  6             11488.77000  11488.65123   0.11877    0.10000   0.09775
11488.70851    0.06149 0.5000
   3:  9  1  9  8  1  8             11488.77000  11488.76579   0.00421    0.10000   0.09775
11488.70851    0.06149 0.5000
   4:  9  7  2  9  8  2             16731.27000  16731.27536  -0.00536    0.10000   0.07088
16731.27513   -0.00513 0.5000
   5:  9  9  1  9  6  3             16731.27000  16731.27490  -0.00490    0.10000   0.07088
16731.27513   -0.00513 0.5000
   6:  10  4  7  9  4  6             15022.28000  15022.34293  -0.06293    0.10000   0.05071
   7:  10  7  3 10  6  5             16704.24000  16704.19779   0.04221    0.10000   0.06608
   8:  11  4  7 10  6  4             16441.28000  16441.29719  -0.01719    0.10000   0.05371
   9:  11  5  7 10  5  6             16495.48000  16495.35230   0.12770    0.10000   0.04964
  10:  11  6  6 10  6  5             16441.28000  16441.27551   0.00449    0.10000   0.05371
  11:  12  0 12 11  0 11             15137.97000  15137.86874   0.10126    0.10000   0.08214
  12:  12  4  8 12  5  8             14565.79000  14565.89261  -0.10261    0.10000   0.05088
  13:  12 12  0 12 11  2             10532.44000  10532.28112   0.15888    0.10000   0.06153
  14:  14  3 11 14  4 11             12286.91000  12287.01219  -0.10219    0.10000   0.07335
  15:  16 10  7 15  9  7             12434.88000  12434.98259  -0.10259    0.10000   0.08782
  16:  17  3 14 16  4 12             12271.85000  12271.97336  -0.12336    0.10000   0.08727
  17:  20 15  6 19 14  6             16804.03000  16803.93894   0.09106    0.10000   0.09179
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  7.03643E-001    3  9.26018E-001    4  1.32055E-001    5  2.12669E-001
6  2.75650E-002
   7  8.28099E-002    8  6.41196E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                        NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A        1729.2085(151)         -0.0000
   2        20000         B         862.1585(121)          0.0000
   3        30000         C         609.0836(138)         -0.0000
   4          200    -DeltaJ          -0.571( 63)E-03       -0.000E-03
   5         2000    -DeltaK          -2.537( 95)E-03        0.000E-03
   6         1100    -DeltaJK          0.827(164)E-03        0.000E-03
   7        40100     -deltaJ          0.1757(250)E-03     -0.0000E-03
   8        41000     -deltaK         -0.403( 54)E-03      -0.000E-03
 MICROWAVE AVG =       -0.002933 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.093063 MHz, IR RMS =        0.00000
```

wwwdu SPFIT Output

```
                          EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  5  5  0  4  4  0             12271.85000   12271.64124    0.20876    0.10000   0.07192
   2:  5  5  1  4  4  1             12349.90000   12350.10573   -0.20573    0.10000   0.07288
   3:  6  3  4  5  2  3             10660.49000   10660.53601   -0.04601    0.10000   0.09882
   4:  6  4  2  5  4  1             12815.64000   12815.61000    0.03000    0.10000   0.09950
   5:  7  3  4  6  4  3             13000.80000   13000.76827    0.03173    0.10000   0.09944
   6:  7  4  4  6  3  4             16793.74000   16793.74889   -0.00889    0.10000   0.09995
   7:  8  6  2  7  6  1             17192.21000   17192.22546   -0.01546    0.10000   0.09987
   8:  8  7  2  7  7  1             16296.69000   16296.68508    0.00492    0.10000   0.09999
   9:  11  0 11 10  0 10               15065.50000   15065.49952    0.00048    0.10000   0.10000
15065.49952    0.00048 0.2500
  10:  11  0 11 10  1 10               15065.50000   15065.49952    0.00048    0.10000   0.10000
15065.49952    0.00048 0.2500
  11:  11  1 11 10  0 10               15065.50000   15065.49952    0.00048    0.10000   0.10000
15065.49952    0.00048 0.2500
  12:  11  1 11 10  1 10               15065.50000   15065.49952    0.00048    0.10000   0.10000
15065.49952    0.00048 0.2500
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  9.64513E-001    3  3.34215E-001    4  6.82401E-002    5  9.31181E-001
6  6.65589E-003
   7  1.35614E-001    8  9.99968E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A        1255.535( 76)          -0.000
   2        20000          B        1153.572( 40)          -0.000
   3        30000          C        660.8078(285)           0.0000
   4          200    -DeltaJ           -2.05(106)E-03         0.00E-03
   5         2000     -DeltaK            1.32(192)E-03         0.00E-03
   6         1100    -DeltaJK          -1.66(299)E-03        -0.00E-03
   7        40100     -deltaJ            0.46( 49)E-03         0.00E-03
   8        41000     -deltaK        -0.01121(307)         -0.00000
 MICROWAVE AVG =       -0.000021 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.100150 MHz, IR RMS =        0.00000
```

wwwud SPFIT Output

```
                          EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  5  2  5  4  2              14458.78000   14458.91314   -0.13314    0.10000   0.08898
   2:   7  4  3  6  3  3              16692.42000   16692.53720   -0.11720    0.10000   0.09158
   3:   7  4  4  6  3  4              16770.32000   16770.08834    0.23166    0.10000   0.06079
   4:  11  1 10 10  2  9                16385.84000   16385.84022   -0.00022    0.10000   0.10000
16385.84022   -0.00022 0.5000
   5:  11  2 10 10  1  9                16385.84000   16385.84022   -0.00022    0.10000   0.10000
16385.84022   -0.00022 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  4.83131E-001    3  9.91162E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                     NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
  1        10000         A       1243.0585(207)         -0.0000
  2        20000         B       1159.4174(146)          0.0000
  3        30000         C        672.9998( 53)          0.0000
 MICROWAVE AVG =       -0.004724 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.145882 MHz, IR RMS =        0.00000
```

wwwwu SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  4  4  1  3  3  1              14867.89000   14867.88669    0.00331    0.10000   0.09473
   2:  6  1  5  5  1  4              11677.20000   11677.13717    0.06283    0.10000   0.08512
   3:  6  5  1  5  2  3              16746.88000   16746.82925    0.05075    0.10000   0.08609
   4:  10  0 10  9  0  9              16237.52000   16237.74034   -0.22034    0.10000   0.05927
16237.64319   -0.12319 0.5000
   5:  10  1 10  9  1  9              16237.52000   16237.54604   -0.02604    0.10000   0.05927
16237.64319   -0.12319 0.5000
   6:  12 12  0 12  5  8              13712.52000   13712.49318    0.02682    0.10000   0.09319
   7:  13  2 11 13  2 12              16196.74000   16196.69692    0.04308    0.10000   0.06905
   8:  13  3 11 13  1 12              16201.69000   16201.76715   -0.07715    0.10000   0.06907
   9:  13 12  2 12  5  8              15475.25000   15475.19984    0.05016    0.10000   0.09367
  10:  14 13  2 13 12  2              16793.74000   16793.77472   -0.03472    0.10000   0.08372
  11:  15  3 12 14  4 10              14867.89000   14867.86525    0.02475    0.10000   0.09656
  12:  16  5 11 16  6 11              15071.44000   15071.44061   -0.00061    0.10000   0.09761
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  9.38957E-001    3  2.24051E-001    4  9.69040E-001    5  1.01744E-001
6  8.35363E-003
   7  1.27580E-001    8  4.19988E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000        A        1976.7127(236)          0.0000
   2        20000        B        1215.700( 32)          -0.000
   3        30000        C        775.4488(128)           0.0000
   4          200    -DeltaJ         -0.911(132)E-03       -0.000E-03
   5         2000    -DeltaK            2.29( 53)E-03        -0.00E-03
   6         1100    -DeltaJK          -1.10( 64)E-03         0.00E-03
   7        40100    -deltaJ         -0.365(144)E-03        0.000E-03
   8        41000    -deltaK            3.05( 51)E-03        -0.00E-03
 MICROWAVE AVG =        0.002367 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.056061 MHz, IR RMS =        0.00000
```

wwwwd SPFIT Output

```
                        EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   5  3  2  4  2  2            14606.25000   14606.15486    0.09514    0.10000   0.09426
   2:   5  4  1  4  4  0            10516.02000   10516.26003   -0.24003    0.10000   0.05387
   3:   9  0  9  8  0  8            14945.49000   14945.46759    0.02241    0.10000   0.09969
   4:   9  9  0  8  8  0            15303.33000   15303.23020    0.09980    0.10000   0.09367
   5:  12  4  8 11  5  6             16057.32000   16057.29490    0.02510    0.10000   0.09961
   6:  12  6  6 12  5  8             12945.01000   12945.02950   -0.01950    0.10000   0.09977
   7:  13 11  3 12 10  3              16495.48000   16495.53205   -0.05205    0.10000   0.09832
   8:  15 14  1 15 13  3              13234.95000   13234.96447   -0.01447    0.10000   0.09988
   9:  20  7 14 20  6 14              16044.26000   16044.24918    0.01082    0.10000   0.09991
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  1.69338E-001    3  1.00000E+000    4  6.24106E-001    5  2.46660E-001
6  2.32349E-002
   7  3.13430E-001    8  3.91021E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A       1946.6638(200)         -0.0000
   2        20000         B       1235.5594( 94)         -0.0000
   3        30000         C        790.6707(135)          0.0000
   4          200    -DeltaJ           0.701(118)E-03        0.000E-03
   5         2000     -DeltaK            5.75( 37)E-03         0.00E-03
   6         1100    -DeltaJK           -8.22( 48)E-03        -0.00E-03
   7        40100     -deltaJ          -0.827( 61)E-03       -0.000E-03
   8        41000     -deltaK           6.659(275)E-03        0.000E-03
 MICROWAVE AVG =       -0.008086 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.094970 MHz, IR RMS =        0.00000
```

D4_uduud SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  11  7  4 10  6  4            12390.74000  12390.77150  -0.03150   0.10000  0.04583
   2:  12  7  5 11  7  4            11532.27000  11532.20620   0.06380   0.10000  0.05283
   3:  13  9  4 12  8  4            14641.35000  14641.35110  -0.00110   0.10000  0.04129
   4:  13 10  4 12  9  4             14642.32000  14642.41037  -0.09037   0.10000  0.04369
   5:  13 13  0 12 12  1              14758.17000  14758.16240   0.00760   0.10000   0.09927
   6:  14  4 10 13  3 10              15774.66000  15774.61313   0.04687   0.10000   0.07031
   7:  14  8  7 13  7  6            12898.91000  12898.88257   0.02743   0.10000  0.04946
   8:  14 11  3 13 10  4              17250.80000  17250.78883   0.01117   0.10000   0.09945
   9:  16  6 11 15  5 10              13381.14000  13381.18346  -0.04346   0.10000   0.06116
  10:  17  9  8 16  9  7             15837.43000  15837.39254   0.03746   0.10000   0.05448
15837.39255    0.03745 0.5000
  11:  17 10  8 16  9  7              15837.43000   15837.39255   0.03745   0.10000   0.05448
15837.39255    0.03745 0.5000
  12:  18  7 11 17  7 10               15635.19000   15635.21512   -0.02512   0.10000   0.04639
15635.21512   -0.02512 0.5000
  13:  18  8 11 17  7 10               15635.19000   15635.21512   -0.02512   0.10000   0.04639
15635.21512   -0.02512 0.5000
  14:  19  8 11 18  8 10               16762.32000   16762.32033   -0.00033   0.10000   0.07128
  15:  20  5 16 19  4 15               15675.25000   15675.27265   -0.02265   0.10000   0.05525
  16:  21  0 21 20  0 20               14588.93000   14588.92178    0.00822   0.10000   0.09959
14588.92178    0.00822 0.5000
  17:  21  1 21 20  0 20               14588.93000   14588.92178    0.00822   0.10000   0.09959
14588.92178    0.00822 0.5000
  18:  22  4 18 21  4 17               17043.73000   17043.71736    0.01264   0.10000   0.08625
  19:  29 23  7 30 14 16                11857.85000   11857.84980    0.00020   0.10000   0.09999
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  1.87293E-001   3  6.81362E-002   4  9.20200E-001   5  2.60338E-001
6  1.36467E-002
   7  4.23302E-001   8  5.22129E-002
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                  NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A        568.0733(130)          0.0000
   2        20000         B        558.7972( 79)          0.0000
   3        30000         C        342.0587( 81)          0.0000
   4          200    -DeltaJ            0.5(107)E-06         -0.0E-06
   5         2000     -DeltaK         -0.2005(275)E-03       0.0000E-03
   6         1100    -DeltaJK           0.232( 36)E-03       -0.000E-03
   7        40100     -deltaJ          0.0398(191)E-03      -0.0000E-03
   8        41000     -deltaK           -3.73( 59)E-03         0.00E-03
 MICROWAVE AVG =        0.000053 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.036249 MHz, IR RMS =        0.00000
```

D4_wudud SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  8  6  3  7  5  3             11215.08000   11215.07709    0.00291    0.10000   0.00000
   2:  8  6  3  7  5  3             11215.08000   11215.07709    0.00291    0.10000   0.00000
   3:  9  3  6  8  2  6             11501.14000   11501.14541   -0.00541    0.10000   0.00000
   4:  9  9  1  8  8  1             13945.15000   13945.15363   -0.00363    0.10000   0.00000
   5:  12  5  7 11  4  7             14982.40000   14982.39474    0.00526    0.10000   0.00000
   6:  12 11  2 11 10  2              18112.50000   18112.49799    0.00201    0.10000   0.00000
   7:  13  1 12 12  1 11              11308.88000   11308.84339    0.03661    0.10000   0.00000
11308.84592    0.03408 0.5000
   8:  13  2 12 12  1 11              11308.88000   11308.84845    0.03155    0.10000   0.00000
11308.84592    0.03408 0.5000
   9:  15  3 12 14  3 11              13962.24000   13962.03362    0.20638    0.10000   0.00000
13962.27953   -0.03953 0.5000
  10:  15  4 12 14  3 11               13962.24000   13962.52543   -0.28543    0.10000   0.00000
13962.27953   -0.03953 0.5000
  11:  19  0 19 18  0 18               15661.28000   15661.29429   -0.01429    0.10000   0.00000
15661.29429   -0.01429 0.5000
  12:  19  1 19 18  0 18               15661.28000   15661.29429   -0.01429    0.10000   0.00000
15661.29429   -0.01429 0.5000
  13:  20  2 18 19  2 17               17492.22000   17492.20154    0.01846    0.10000   0.00000
17492.20155    0.01845 0.5000
  14:  20  3 18 19  2 17               17492.22000   17492.20156    0.01844    0.10000   0.00000
17492.20155    0.01845 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  9.75160E-001    3  2.54893E-001    4  8.97902E-002    5  9.98066E-001
6  1.17145E-002
   7  2.66032E-001    8  6.44877E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
  1        10000          A        790.7318(108)         -0.0000
  2        20000          B        575.1071(104)          0.0000
  3        30000          C        405.4978( 67)         -0.0000
  4          200    -DeltaJ           0.115( 36)E-03       -0.000E-03
  5         2000    -DeltaK             1.361(195)E-03       -0.000E-03
  6         1100    -DeltaJK          -1.557(222)E-03        0.000E-03
  7        40100     -deltaJ         -0.0288(213)E-03      -0.0000E-03
  8        41000     -deltaK            0.282(231)E-03       -0.000E-03
 MICROWAVE AVG =        0.000276 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.018328 MHz, IR RMS =        0.00000
```

D4_wuudu SPFIT Output

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  7  7  1  6  6  1              10744.88000   10744.88292   -0.00292    0.10000   0.00000
   2:  7  7  1  6  6  1              10744.88000   10744.88292   -0.00292    0.10000   0.00000
   3:  9  8  2  8  7  2              13342.25000   13342.23748    0.01252    0.10000   0.00000
   4:  10  7  4  9  6  4              13829.39000   13829.39713   -0.00713    0.10000   0.00000
   5:  11 11  1 10 10  1              17046.32000   17046.32173   -0.00173    0.10000   0.00000
   6:  15  1 14 14  1 13              12662.51000   12662.52180   -0.01180    0.10000   0.00000
12662.52181   -0.01181 0.5000
   7:  15  2 14 14  1 13              12662.51000   12662.52182   -0.01182    0.10000   0.00000
12662.52181   -0.01181 0.5000
   8:  16  0 16 15  0 15              12891.15000   12891.18438   -0.03438    0.10000   0.00000
12891.18438   -0.03438 0.5000
   9:  16  1 16 15  0 15              12891.15000   12891.18438   -0.03438    0.10000   0.00000
12891.18438   -0.03438 0.5000
  10:  18  1 17 17  1 16              15025.59000   15025.50894    0.08106    0.10000   0.00000
15025.50894    0.08106 0.5000
  11:  18  2 17 17  1 16              15025.59000   15025.50894    0.08106    0.10000   0.00000
15025.50894    0.08106 0.5000
  12:  19  5 14 18  5 13              18081.09000   18081.00531    0.08469    0.10000   0.00000
18081.08400    0.00600 0.5000
  13:  19  6 14 18  5 13              18081.09000   18081.16268   -0.07268    0.10000   0.00000
18081.08400    0.00600 0.5000
  14:  20  2 18 19  2 17              17160.90000   17160.94137   -0.04137    0.10000   0.00000
17160.94137   -0.04137 0.5000
  15:  20  3 18 19  2 17              17160.90000   17160.94137   -0.04137    0.10000   0.00000
17160.94137   -0.04137 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  5.39988E-001   3  1.66235E-001   4  3.31494E-002   5  5.80645E-001
6  3.04726E-003
   7  2.57526E-001   8  9.99697E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A         787.0991(103)          0.0000
   2        20000          B          592.981( 94)          0.000
   3        30000          C         394.2108(112)         -0.0000
   4          200    -DeltaJ           2.089(112)E-03        0.000E-03
   5         2000     -DeltaK            1.62( 71)E-03         0.00E-03
   6         1100    -DeltaJK          -3.87( 79)E-03        -0.00E-03
   7        40100     -deltaJ           0.527( 53)E-03        0.000E-03
   8        41000     -deltaK          -2.79( 79)E-03         0.00E-03
 MICROWAVE AVG =       -0.000268 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.031412 MHz, IR RMS =        0.00000
```

D4_wuduu SPFIT Output

```
                        EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  7  7  1  6  6  1             10842.82000   10842.82015   -0.00015    0.10000   0.00000
   2:  7  7  1  6  6  1             10842.82000   10842.82015   -0.00015    0.10000   0.00000
   3:  10  9  2  9  8  2             15037.50000   15037.49996    0.00004    0.10000   0.00000
   4:  11 11  1 10 10  1              17217.60000   17217.59990    0.00010    0.10000   0.00000
   5:  15  1 14 14  1 13              12741.43000   12741.37297    0.05703    0.10000   0.00000
12741.37301    0.05699 0.5000
   6:  15  2 14 14  1 13              12741.43000   12741.37305    0.05695    0.10000   0.00000
12741.37301    0.05699 0.5000
   7:  16  3 13 15  3 12              14633.90000   14633.91827   -0.01827    0.10000   0.00000
14633.93984   -0.03984 0.5000
   8:  16  4 13 15  3 12              14633.90000   14633.96142   -0.06142    0.10000   0.00000
14633.93984   -0.03984 0.5000
   9:  17  0 17 16  0 16              13787.49000   13787.53856   -0.04856    0.10000   0.00000
13787.53856   -0.04856 0.5000
  10:  17  1 17 16  0 16              13787.49000   13787.53856   -0.04856    0.10000   0.00000
13787.53856   -0.04856 0.5000
  11:  19  4 15 18  4 14              17566.11000   17566.05408    0.05592    0.10000   0.00000
17566.06393    0.04607 0.5000
  12:  19  5 15 18  4 14              17566.11000   17566.07378    0.03622    0.10000   0.00000
17566.06393    0.04607 0.5000
  13:  20  1 19 19  1 18              16713.22000   16713.17914    0.04086    0.10000   0.00000
16713.17914    0.04086 0.5000
  14:  20  2 19 19  1 18              16713.22000   16713.17914    0.04086    0.10000   0.00000
16713.17914    0.04086 0.5000
  15:  20  3 17 19  3 16              17804.33000   17804.38413   -0.05413    0.10000   0.00000
17804.38420   -0.05420 0.5000
  16:  20  4 17 19  3 16              17804.33000   17804.38427   -0.05427    0.10000   0.00000
17804.38420   -0.05420 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  2.25785E-001    3  1.34924E-001    4  2.44986E-002    5  5.96865E-001
6  4.20162E-003
   7  2.58077E-001    8  9.96925E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A         794.7696(117)          0.0000
   2        20000         B          585.089(118)          -0.000
   3        30000         C         397.5055(149)          0.0000
   4          200    -DeltaJ          4.403(108)E-03       -0.000E-03
   5         2000    -DeltaK         0.01432( 44)         -0.00000
   6         1100   -DeltaJK        -0.01861( 50)          0.00000
   7        40100    -deltaJ         -0.293( 59)E-03        0.000E-03
   8        41000    -deltaK         0.01020( 43)         -0.00000
 MICROWAVE AVG =        0.000117 MHz, IR AVG =        0.00000
```

```
MICROWAVE RMS =       0.037313 MHz, IR RMS =       0.00000
```

D4_wdudu SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  9  9  1  8  8  1              13851.28000   13851.29920   -0.01920    0.10000   0.00000
   2:  9  9  1  8  8  1              13851.28000   13851.29920   -0.01920    0.10000   0.00000
   3: 10 10  1  9  9  1               15421.06000   15420.99639    0.06361    0.10000   0.00000
   4:  11 11  1 10 10  1               16990.62000   16990.64648   -0.02648    0.10000   0.00000
   5:  12  2 10 11  2  9              11098.74000   11098.79815   -0.05815    0.10000   0.00000
   6:  13  0 13 12  0 12               10906.82000   10906.83386   -0.01386    0.10000   0.00000
10906.83387   -0.01387 0.5000
   7:  13  1 13 12  0 12               10906.82000   10906.83389   -0.01389    0.10000   0.00000
10906.83387   -0.01387 0.5000
   8:  14  2 12 13  2 11               12734.10000   12734.01918    0.08082    0.10000   0.00000
   9:  19  0 19 18  0 18               15817.40000   15817.44027   -0.04027    0.10000   0.00000
15817.44027   -0.04027 0.5000
  10:  19  1 19 18  0 18                15817.40000   15817.44027   -0.04027    0.10000   0.00000
15817.44027   -0.04027 0.5000
  11:  19  1 18 18  1 17                16318.88000   16318.79207    0.08793    0.10000   0.00000
16318.79207    0.08793 0.5000
  12:  19  2 18 18  1 17                16318.88000   16318.79207    0.08793    0.10000   0.00000
16318.79207    0.08793 0.5000
  13:  19  3 16 18  3 15                17328.21000   17328.32253   -0.11253    0.10000   0.00000
17328.32308   -0.11308 0.5000
  14:  19  4 16 18  3 15                17328.21000   17328.32363   -0.11363    0.10000   0.00000
17328.32308   -0.11308 0.5000
  15:  19  4 15 18  4 14                17839.44000   17839.38787    0.05213    0.10000   0.00000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  2.63529E-001    3  1.44163E-001    4  2.00148E-002    5  7.04968E-001
6  1.12313E-003
   7  1.47727E-001    8  9.97840E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A          785.234( 32)          -0.000
   2        20000          B          577.807(119)           0.000
   3        30000          C        410.0023(105)           0.0000
   4          200    -DeltaJ           1.837(114)E-03       -0.000E-03
   5         2000    -DeltaK          0.01847(186)         -0.00000
   6         1100   -DeltaJK        -0.02075(192)          0.00000
   7        40100     -deltaJ          0.749( 58)E-03       -0.000E-03
   8        41000     -deltaK          0.02174(298)         -0.00000
 MICROWAVE AVG =       -0.000524 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.060639 MHz, IR RMS =        0.00000
```

D4_wduud SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  7  7  1  6  6  1              10553.27000   10553.31651   -0.04651    0.10000   0.00000
   2:  7  7  1  6  6  1              10553.27000   10553.31651   -0.04651    0.10000   0.00000
   3:  8  4  4  7  3  4              10624.71000   10624.72442   -0.01442    0.10000   0.00000
   4:  10  8  3  9  7  3              14225.14000   14225.03952    0.10048    0.10000   0.00000
   5:  11  6  5 10  5  5              14507.79000   14507.79613   -0.00613    0.10000   0.00000
   6:  11 11  1 10 10  1              16713.22000   16713.13200    0.08800    0.10000   0.00000
   7:  12 11  2 11 10  2              17774.87000   17774.97277   -0.10277    0.10000   0.00000
   8:  14  3 12 13  2 11              12233.38000   12233.32256    0.05744    0.10000   0.00000
   9:  15  0 15 14  0 14              11771.15000   11771.10288    0.04712    0.10000   0.00000
11771.10288    0.04712 0.5000
  10:  15  1 15 14  0 14              11771.15000   11771.10288    0.04712    0.10000   0.00000
11771.10288    0.04712 0.5000
  11:  17  0 17 16  0 16              13298.38000   13298.54150   -0.16150    0.10000   0.00000
13298.54150   -0.16150 0.5000
  12:  17  1 17 16  0 16              13298.38000   13298.54150   -0.16150    0.10000   0.00000
13298.54150   -0.16150 0.5000
  13:  19  0 19 18  0 18              14825.58000   14825.54593    0.03407    0.10000   0.00000
14825.54593    0.03407 0.5000
  14:  19  0 19 18  1 18              14825.58000   14825.54593    0.03407    0.10000   0.00000
14825.54593    0.03407 0.5000
  15:  17  3 14 16  3 13              15137.52000   15137.50815    0.01185    0.10000   0.00000
15137.50817    0.01183 0.5000
  16:  17  4 14 16  3 13              15137.52000   15137.50819    0.01181    0.10000   0.00000
15137.50817    0.01183 0.5000
  17:  18  3 16 17  2 15              15286.92000   15286.82873    0.09127    0.10000   0.00000
  18:  20  2 18 19  2 17              16812.92000   16813.02660   -0.10660    0.10000   0.00000
16813.02660   -0.10660 0.5000
  19:  20  3 18 19  2 17              16812.92000   16813.02660   -0.10660    0.10000   0.00000
16813.02660   -0.10660 0.5000
  20:  23  1 23 22  1 22              17878.09000   17878.04784    0.04216    0.10000   0.00000
17878.04784    0.04216 0.5000
  21:  23  0 23 22  1 22              17878.09000   17878.04784    0.04216    0.10000   0.00000
17878.04784    0.04216 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  9.61765E-001    3  2.53278E-001    4  5.76259E-002    5  9.98015E-001
6  8.00406E-003
   7  2.97597E-001    8  7.45278E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                   NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
  1        10000          A        771.0529( 87)          0.0000
  2        20000          B        623.7929(136)         -0.0000
  3        30000          C        382.2803( 44)          0.0000
  4          200    -DeltaJ          -1.375( 45)E-03        0.000E-03
```

```
  5        2000   -DeltaK        -1.734(144)E-03      0.000E-03
  6        1100   -DeltaJK        2.848(182)E-03     -0.000E-03
  7       40100    -deltaJ       0.4463(242)E-03     0.0000E-03
  8       41000    -deltaK       -2.627(230)E-03      0.000E-03
MICROWAVE AVG =      -0.000805 MHz, IR AVG =      0.00000
MICROWAVE RMS =       0.076310 MHz, IR RMS =      0.00000
```

D4_wwduu SPFIT Output

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   8  3  5  7  2  5              12698.86000   12698.85367    0.00633    0.10000   0.09634
   2:   8  4  5  7  3  5              13383.40000   13383.39430    0.00570    0.10000   0.09703
   3:   8  6  3  7  5  3              14592.76000   14592.75944    0.00056    0.10000   0.09997
   4:   9  2  8  8  1  8              15122.06000   15122.05137    0.00863    0.10000   0.09307
   5:   9  3  7  8  2  7              15003.19000   15003.20991   -0.01991    0.10000   0.05363
   6:  10  3  8  9  3  7               11318.19000   11318.19297   -0.00297    0.10000   0.09921
   7:  12  4  8 11  4  7                15023.42000   15023.41897    0.00103    0.10000   0.09992
   8:  13  4 10 12  3  9                 14955.66000   14955.65833    0.00167    0.10000   0.09974
   9:  14  0 14 13  0 13                  13605.03000   13605.03023   -0.00023    0.10000   0.09999
13605.03025   -0.00025 0.5000
  10:  14  1 14 13  0 13                   13605.03000   13605.03027   -0.00027    0.10000   0.09999
13605.03025   -0.00025 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  3.73296E-001   3  1.73101E-001   4  3.16977E-002   5  9.91559E-001
6  5.83192E-003
   7  8.54996E-001   8  5.50536E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A        1049.542( 65)          0.000
   2        20000         B        713.4666(229)         -0.0000
   3        30000         C        472.7719(150)         -0.0000
   4          200    -DeltaJ          -2.08( 36)E-03        0.00E-03
   5         2000     -DeltaK           -6.15(110)E-03        0.00E-03
   6         1100    -DeltaJK            7.70(139)E-03       -0.00E-03
   7        40100      -deltaJ          1.064(229)E-03       0.000E-03
   8        41000      -deltaK           -5.90(112)E-03        0.00E-03
 MICROWAVE AVG =        0.000087 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.007865 MHz, IR RMS =        0.00000
```

D4_wwudu SPFIT Output

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   7  6  2  6  5  2                12731.46000   12731.46005   -0.00005    0.10000   0.10000
   2:  13  2 11 12  2 10                14663.08000   14663.06127    0.01873    0.10000   0.07066
   3:  13  2 11 12  3 10                14662.49000   14662.50870   -0.01870    0.10000   0.07076
   4:  25  3 23 25  2 24                15415.21000   15415.20998    0.00002    0.10000   0.10000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  4.12490E-001    3  7.79589E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                     NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A        985.4447(102)         -0.0000
   2        20000         B        725.1953( 67)         -0.0000
   3        30000         C       500.20201(278)         -0.00000
 MICROWAVE AVG =       -0.000002 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.013233 MHz, IR RMS =        0.00000
```

D4_wwdud SPFIT Output

```
                        EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  6  0  5  5  0              11260.56000   11260.77672   -0.21672    0.10000   0.07107
11260.51443    0.04557 0.5000
   2:   6  6  1  5  5  0              11260.56000   11260.25215    0.30785    0.10000   0.07107
11260.51443    0.04557 0.5000
   3:   6  6  1  5  5  1              11262.51000   11262.55602   -0.04602    0.10000   0.07037
   4:   8  7  2  7  6  2              14482.99000   14482.98976    0.00024    0.10000   0.10000
   5:   9  5  5  8  5  4              11755.02000   11755.02025   -0.00025    0.10000   0.10000
   6:  10  2  8  9  3  7               11866.66000   11866.65912    0.00088    0.10000   0.09986
   7:  10  3  7  9  2  7               16413.86000   16413.85962    0.00038    0.10000   0.10000
   8:  10  3  8  9  2  7               11880.92000   11880.92024   -0.00024    0.10000   0.10013
   9:  11  3  8 10  3  7                13576.86000   13576.86057   -0.00057    0.10000   0.09999
  10:  11  4  7 10  3  7                17888.10000   17888.10008   -0.00008    0.10000   0.09999
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  8.37657E-001    3  3.14849E-001    4  1.00222E-001    5  1.20894E-001
6  4.08107E-003
   7  1.62530E-001    8  9.99330E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A         964.962(133)           0.000
   2        20000         B        739.7062(288)           0.0000
   3        30000         C         513.243( 43)           0.000
   4          200    -DeltaJ          1.23(125)E-03        -0.00E-03
   5         2000     -DeltaK            7.0( 40)E-03        -0.0E-03
   6         1100    -DeltaJK           -7.4( 51)E-03          0.0E-03
   7        40100     -deltaJ          -0.98( 70)E-03         0.00E-03
   8        41000     -deltaK            7.3( 57)E-03         -0.0E-03
 MICROWAVE AVG =       -0.000011 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.021592 MHz, IR RMS =        0.00000
```

D4_wwuud SPFIT Output

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   7  1  6  6  0  6              11872.92000   11872.93144   -0.01144    0.10000   0.09984
   2:   7  2  6  6  1  6              11888.27000   11888.25873    0.01127    0.10000   0.09996
   3:   8  6  3  7  5  3              14584.00000   14583.99985    0.00015    0.10000   0.10000
   4:   9  3  6  8  2  6              14833.87000   14833.86902    0.00098    0.10000   0.09999
   5:  10  1  9  9  1  8               10494.12000   10493.93987    0.18013    0.10000   0.07110
   6:  10  2  8  9  3  7               11262.51000   11262.51681   -0.00681    0.10000   0.09986
   7:  10  2  9  9  1  8               10494.12000   10494.30139   -0.18139    0.10000   0.07067
   8:  12  1 11 11  2 10                  12355.83000   12355.81100    0.01900    0.10000   0.10036
12355.82285    0.00715 0.5000
   9:  12  2 11 11  2 10                  12355.83000   12355.83471   -0.00471    0.10000   0.10036
12355.82285    0.00715 0.5000
  10:  19  0 19 18  1 18                  18092.02000   18092.02072   -0.00072    0.10000   0.09992
18092.02072   -0.00072 0.5000
  11:  19  1 19 18  1 18                  18092.02000   18092.02072   -0.00072    0.10000   0.09992
18092.02072   -0.00072 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  1.05371E-001    3  2.73420E-001    4  2.76957E-003    5  9.98288E-001
6  2.05202E-004
   7  9.46740E-001    8  5.76492E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
  1        10000          A          1045.20( 47)           -0.00
  2        20000          B          727.431(175)           0.000
  3        30000          C          466.294( 43)          -0.000
  4          200    -DeltaJ            -7.0( 37)E-03         -0.0E-03
  5         2000    -DeltaK          -0.0221(143)          -0.0000
  6         1100   -DeltaJK           0.0285(178)           0.0000
  7        40100    -deltaJ           4.12(236)E-03         0.00E-03
  8        41000    -deltaK          -0.0245(155)          -0.0000
 MICROWAVE AVG =       -0.000076 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.085443 MHz, IR RMS =        0.00000
```

D4_wuwuu SPFIT Output

```
                      EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   7  2  6  6  1  6              11376.50000   11376.49687    0.00313    0.10000   0.10000
   2:   9  6  4  8  5  4              15855.49000   15855.49275   -0.00275    0.10000   0.10000
   3:  12  3 10 11  3  9               12795.59000   12795.47051    0.11949    0.10000   0.08761
   4:  13  4 10 12  4  9               14433.87000   14433.94520   -0.07520    0.10000   0.09553
   5:  14  3 12 13  2 11               14625.11000   14625.25173   -0.14173    0.10000   0.08420
   6:  16  3 13 15  4 12               17180.91000   17180.79227    0.11773    0.10000   0.09279
   7:  16  4 13 15  3 12               17196.79000   17196.71326    0.07674    0.10000   0.09269
   8:  17  3 14 16  3 13               18097.03000   18096.94928    0.08072    0.10000   0.06703
   9:  17  4 14 16  4 13               18094.00000   18094.18842   -0.18842    0.10000   0.06656
  10:  18  1 17 17  1 16               17527.66000   17527.64577    0.01423    0.10000   0.10033
17527.64597    0.01403 0.5000
  11:  18  2 17 17  1 16               17527.66000   17527.64617    0.01383    0.10000   0.10033
17527.64597    0.01403 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  6.14682E-001    3  1.76946E-001    4  2.68423E-003    5  9.38945E-001
6  9.54786E-005
   7  4.23325E-001    8  5.74557E-002
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                   NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A          1068.31(184)           -0.01
   2        20000          B           673.87( 55)           0.00
   3        30000          C          457.357( 41)           0.000
   4          200    -DeltaJ           0.0344(113)           0.0000
   5         2000    -DeltaK           0.0505(206)           0.0001
   6         1100    -DeltaJK         -0.086( 32)           -0.000
   7        40100     -deltaJ         -0.0232( 72)          -0.0000
   8        41000     -deltaK          0.0386(168)           0.0001
 MICROWAVE AVG =        0.000374 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.100996 MHz, IR RMS =        0.00000
```

D4_wuwdu SPFIT Output

```
                      EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  11  4  8 10  3  8                17354.08000   17354.06345    0.01655    0.10000   0.09997
   2:  13  2 12 12  1 11                12947.63000   12947.03373    0.59627    0.10000   0.05774
   3:  14  1 14 13  0 13                13149.78000   13149.92107   -0.14107    0.10000   0.09813
   4:  15  2 13 14  3 12                15486.79000   15487.18724   -0.39724    0.10000   0.08385
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  3.00086E-002    3  9.82319E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A          1083.57( 61)            0.00
   2        20000         B         656.876(160)           -0.000
   3        30000         C        456.9931( 46)          -0.0000
 MICROWAVE AVG =        0.018629 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.365210 MHz, IR RMS =        0.00000
```

D4_wuwud SPFIT Output

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   9  2  7  8  1  7              13902.63000   13902.25653    0.37347    0.10000   0.08355
   2:  10  4  7  9  3  7               15719.56000   15719.97422   -0.41422    0.10000   0.08123
   3:  13  3 11 12  2 10                13566.34000   13565.71795    0.62205    0.10000   0.05899
   4:  13  4 10 12  3  9               14576.25000   14575.97043    0.27957    0.10000   0.08521
   5:  15  2 13 14  2 12                15347.45000   15348.17941   -0.72941    0.10000   0.07545
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  6.61543E-001    3  8.66810E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A       1092.6220(217)         -0.0000
   2        20000         B         646.5223( 54)          0.0000
   3        30000         C         452.4241( 34)         -0.0000
 MICROWAVE AVG =        0.026292 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.511508 MHz, IR RMS =        0.00000
```

D4_wwuwd SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   5  4  2  4  3  2                13622.12000   13622.12006   -0.00006    0.10000   0.10000
   2:   7  3  5  6  2  5                14741.29000   14741.29754   -0.00754    0.10000   0.09975
   3:   9  2  8  8  2  7                11235.09000   11235.07411    0.01589    0.10000   0.09888
   4:   9  3  7  8  2  7                18073.97000   18073.96185    0.00815    0.10000   0.09971
   5:  10  1 10  9  0  9                 11498.95000   11498.94818    0.00182    0.10000   0.09999
   6:  11  2  9 10  3  8                 13131.24000   13131.28710   -0.04710    0.10000   0.08965
   7:  12  3 10 11  2  9                  16548.29000   16548.33788   -0.04788    0.10000   0.08928
   8:  12  3 10 11  3  9                  15434.38000   15434.30002    0.07998    0.10000   0.06587
   9:  14  2 13 13  2 12                   16835.51000   16835.51348   -0.00348    0.10000   0.09995
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  1.50716E-001    3  8.76886E-001    4  3.83819E-002    5  3.35732E-001
6  1.09222E-003
   7  9.96737E-001    8  2.57714E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A         1664.241(155)           -0.000
   2        20000          B          750.043( 40)           0.000
   3        30000          C         550.7996( 90)           0.0000
   4          200    -DeltaJ            4.09(276)E-03         0.00E-03
   5         2000    -DeltaK             5.0( 51)E-03          0.0E-03
   6         1100    -DeltaJK           -9.2( 78)E-03         -0.0E-03
   7        40100     -deltaJ          -1.60(150)E-03        -0.00E-03
   8        41000     -deltaK            1.1( 32)E-03          0.0E-03
 MICROWAVE AVG =       -0.000023 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.035434 MHz, IR RMS =        0.00000
```

D4_wwwud SPFIT Output

```
                          EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  5  1  4  4  0  4               10900.36000   10900.39500   -0.03500    0.10000   0.09448
   2:  6  4  3  5  3  3               13074.53000   13074.44476    0.08524    0.10000   0.06023
   3:  7  3  4  6  4  3               11953.61000   11953.64074   -0.03074    0.10000   0.09580
   4:  8  3  5  7  2  5               17433.97000   17434.01090   -0.04090    0.10000   0.09234
   5:  8  3  5  7  4  4               13193.78000   13193.72226    0.05774    0.10000   0.09930
13193.76824    0.01176 0.5000
   6:  8  4  5  7  4  4               13193.78000   13193.81421   -0.03421    0.10000   0.09930
13193.76824    0.01176 0.5000
   7:  8  8  0  7  7  0               17682.83000   17682.83084   -0.00084    0.10000   0.09999
   8:  10  3  7  9  3  6               15663.20000   15663.18790    0.01210    0.10000   0.09928
15663.18814    0.01186 0.5000
   9:  10  4  7  9  3  6               15663.20000   15663.18838    0.01162    0.10000   0.09928
15663.18814    0.01186 0.5000
  10:  15  5 11 15  3 12                10856.23000   10856.22655    0.00345    0.10000   0.10002
10856.22655    0.00345 0.5000
  11:  15  5 11 15  4 12                10856.23000   10856.22655    0.00345    0.10000   0.10002
10856.22655    0.00345 0.5000
  12:  18  8 11 18  7 12                10842.81000   10842.81152   -0.00152    0.10000   0.10057
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  1.12460E-002    3  1.56334E-001    4  8.13395E-001    5  2.84001E-001
6  4.86962E-003
   7  9.97725E-001    8  4.70601E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                     NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A          1112.59( 78)            0.00
   2        20000          B          1068.93( 68)           -0.00
   3        30000          C        617.9649(246)           0.0000
   4          200    -DeltaJ          -1.059(308)E-03        0.000E-03
   5         2000    -DeltaK            -9.66(170)E-03         0.00E-03
   6         1100   -DeltaJK         0.01032(207)        -0.00000
   7        40100     -deltaJ         -0.0165( 35)          0.0000
   8        41000     -deltaK         -0.0659( 93)          0.0000
 MICROWAVE AVG =        0.000368 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.035594 MHz, IR RMS =        0.00000
```

D4_wwdwd SPFIT Output

```
                          EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   9  2  8  8  1  8               18080.84000   18080.84041   -0.00041    0.10000   0.10000
   2:  10  0 10  9  1  9                11865.03000   11864.97617    0.05383    0.10000   0.07198
   3:  10  1 10  9  0  9                11872.92000   11872.97579   -0.05579    0.10000   0.06946
   4:  13  3 11 12  2 10                 17374.42000   17374.41821    0.00179    0.10000   0.09997
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  4.38800E-001    3  9.54873E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
  1        10000         A        1540.465( 52)          -0.000
  2        20000         B        780.6484(114)           0.0000
  3        30000         C        570.8311( 38)          -0.0000
 MICROWAVE AVG =       -0.000144 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.038774 MHz, IR RMS =        0.00000
```

D4_wwwdd SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   7  6  1  6  5  1              15490.73000   15490.61214    0.11786    0.10000   0.06934
   2:   8  3  6  7  2  6              17683.89000   17684.00244   -0.11244    0.10000   0.07385
   3:  10  5  5  9  6  4              17393.62000   17393.61102    0.00898    0.10000   0.05832
   4:  10  5  6  9  4  5              16437.25000   16437.27515   -0.02515    0.10000   0.08270
   5:  10  6  4  9  7  3              17774.87000   17774.84638    0.02362    0.10000   0.09746
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  7.57617E-001    3  9.91303E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
  1        10000        A       1169.3579( 67)          0.0000
  2        20000        B       1050.6906( 44)         -0.0000
  3        30000        C        586.4166( 88)          0.0000
 MICROWAVE AVG =        0.002574 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.074572 MHz, IR RMS =        0.00000
```

D4_wwdwu SPFIT Output

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  1  5  5  0  5               11162.50000   11162.37368    0.12632    0.10000   0.08601
   2:   7  3  5  6  2  5               14651.32000   14651.36764   -0.04764    0.10000   0.09813
   3:  12  1 12 11  1 11                  13605.03000   13604.88834    0.14166    0.10000   0.08202
   4:  14  2 12 13  3 11                  17393.62000   17393.77174   -0.15174    0.10000   0.07902
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  8.39711E-001    3  9.98053E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
  1        10000         A       1653.2342(247)          -0.0000
  2        20000         B         746.0877( 51)           0.0000
  3        30000         C         547.3222( 36)          -0.0000
 MICROWAVE AVG =        0.017151 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.123813 MHz, IR RMS =        0.00000
```

D4_wwuwu SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  3  4  5  2  4                 12891.14000   12891.15058   -0.01058    0.10000   0.09999
   2:  10  2  9  9  1  8                 12718.20000   12718.02126    0.17874    0.10000   0.09755
   3:  10  3  8  9  3  7                 13189.64000   13189.11694    0.52306    0.10000   0.07580
   4:  12  3 10 11  3  9                 15590.68000   15591.25943   -0.57943    0.10000   0.06904
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  6.24299E-001    3  9.42117E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A        1579.4473(261)          -0.0000
   2        20000         B         763.2353(126)           0.0000
   3        30000         C         557.7811( 49)          -0.0000
 MICROWAVE AVG =        0.027947 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.400436 MHz, IR RMS =        0.00000
```

D4_wwwwd SPFIT Output

```
                          EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   3  3  1  2  2  1              10561.49000   10561.45656    0.03344    0.10000   0.09821
   2:   6  1  5  5  2  4              10442.81000   10442.68505    0.12495    0.10000   0.07100
   3:   7  3  5  6  3  4              13309.46000   13309.58143   -0.12143    0.10000   0.07291
   4:  16  4 13 16  2 14                17176.64000   17176.64243   -0.00243    0.10000   0.09999
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  7.00067E-001    3  5.35856E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                     NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A       1911.5654(200)          0.0000
   2        20000         B       1134.5525( 63)         -0.0000
   3        30000         C        747.9365( 55)         0.0000
 MICROWAVE AVG =        0.008631 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.088713 MHz, IR RMS =        0.00000
```

D4_wwwwu SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  4  1  3  3  0  3            10442.81000  10442.91486  -0.10486   0.10000  0.09505
   2:  4  4  0  3  3  0            14550.84000  14550.77842   0.06158   0.10000  0.09832
   3:  7  1  6  6  1  5            12449.21000  12449.41991  -0.20991   0.10000  0.07831
   4:  7  1  6  6  2  5            11985.73000  11985.49526   0.23474   0.10000  0.07187
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  9.20356E-001    3  9.93595E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                  NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1       10000       A      1945.6061(142)          0.0000
   2       20000       B      1113.5160(102)         -0.0000
   3       30000       C       732.6576( 77)          0.0000
 MICROWAVE AVG =      -0.004613 MHz, IR AVG =       0.00000
 MICROWAVE RMS =       0.168786 MHz, IR RMS =       0.00000
```

D2O_wdudu SPFIT Output

```
                     EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  7  4  4  6  3  4              10701.77000   10701.76973    0.00027    0.10000   0.00000
   2:  7  4  4  6  3  4              10701.77000   10701.76973    0.00027    0.10000   0.00000
   3:  8  6  3  7  5  3              12705.98000   12705.99022   -0.01022    0.10000   0.00000
   4:  9  6  4  8  5  4              13952.61000   13952.58894    0.02106    0.10000   0.00000
   5:  9  8  2  8  7  2              15025.84000   15025.84027   -0.00027    0.10000   0.00000
   6:  10  6  5  9  5  5              15262.50000   15262.51275   -0.01275    0.10000   0.00000
   7:  11  1 10 10  1  9              11128.03000   11127.98108    0.04892    0.10000   0.00000
11127.98555    0.04445 0.5000
   8:  11  2 10 10  1  9              11128.03000   11127.99001    0.03999    0.10000   0.00000
11127.98555    0.04445 0.5000
   9:  14  0 14 13  0 13              13306.15000   13306.15252   -0.00252    0.10000   0.00000
13306.15252   -0.00252 0.5000
  10:  14  1 14 13  0 13              13306.15000   13306.15252   -0.00252    0.10000   0.00000
13306.15252   -0.00252 0.5000
  11:  14  1 13 13  1 12              13912.51000   13912.56045   -0.05045    0.10000   0.00000
13912.56048   -0.05048 0.5000
  12:  14  2 13 13  1 12              13912.51000   13912.56052   -0.05052    0.10000   0.00000
13912.56048   -0.05048 0.5000
  13:  17  3 14 16  3 13              17912.49000   17912.48163    0.00837    0.10000   0.00000
17912.48259    0.00741 0.5000
  14:  17  4 14 16  3 13              17912.49000   17912.48354    0.00646    0.10000   0.00000
17912.48259    0.00741 0.5000
  15:  19  0 19 18  0 18              17945.32000   17945.31235    0.00765    0.10000   0.00000
17945.31235    0.00765 0.5000
  16:  19  1 19 18  0 18              17945.32000   17945.31235    0.00765    0.10000   0.00000
17945.31235    0.00765 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  2.23809E-001    3  2.81865E-001    4  3.34117E-002    5  9.97202E-001
6  1.44996E-003
   7  8.83935E-001    8  5.65206E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1         10000          A          882.460(100)           0.000
   2         20000          B          684.232( 68)          -0.000
   3         30000          C         464.5505( 75)          0.0000
   4           200    -DeltaJ          1.462(309)E-03        0.000E-03
   5          2000    -DeltaK            4.84(179)E-03        0.00E-03
   6          1100   -DeltaJK           -6.68(209)E-03       -0.00E-03
   7         40100    -deltaJ          -1.813(309)E-03       0.000E-03
   8         41000    -deltaK            6.64(197)E-03        0.00E-03
 MICROWAVE AVG =       0.000443 MHz, IR AVG =       0.00000
 MICROWAVE RMS =       0.022065 MHz, IR RMS =       0.00000
```

D2O_wuduu SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   7  6  2  6  5  2              11601.34000   11601.35505   -0.01505    0.10000   0.06431
   2:   7  6  2  6  5  2              11601.34000   11601.35505   -0.01505    0.10000   0.06431
   3:   7  7  1  6  6  1              12194.86000   12194.85713    0.00287    0.10000   0.09993
   4:   8  5  4  7  4  4              12387.75000   12387.75328   -0.00328    0.10000   0.09967
   5:   8  7  2  7  6  2              13380.26000   13380.21729    0.04271    0.10000   0.05405
   6:   9  8  2  8  7  2              15162.50000   15162.51739   -0.01739    0.10000   0.09414
   7:  11  0 11 10  0 10                10287.48000   10287.48634   -0.00634    0.10000   0.09965
10287.48639   -0.00639 0.5000
   8:  11  1 11 10  0 10                10287.48000   10287.48643   -0.00643    0.10000   0.09965
10287.48639   -0.00639 0.5000
   9:  14  2 12 13  2 11                14289.15000   14289.09977    0.05023    0.10000   0.06426
14289.10204    0.04796 0.5000
                                        14289.15000   14289.10431    0.04569    0.10000   0.06426
  10:  14  3 12 13  2 11
14289.10204    0.04796 0.5000
  11:  15  1 14 14  1 13                14550.83000   14550.86443   -0.03443    0.10000   0.08006
14550.86443   -0.03443 0.5000
  12:  15  2 14 14  1 13                14550.83000   14550.86444   -0.03444    0.10000   0.08006
14550.86443   -0.03443 0.5000
  13:  17  3 14 16  3 13                17650.81000   17650.82052   -0.01052    0.10000   0.09857
17650.82148   -0.01148 0.5000
  14:  17  4 14 16  3 13                17650.81000   17650.82245   -0.01245    0.10000   0.09857
17650.82148   -0.01148 0.5000
  15:  19  0 19 18  0 18                17530.50000   17530.49251    0.00749    0.10000   0.09919
17530.49251    0.00749 0.5000
  16:  19  1 19 18  0 18                17530.50000   17530.49251    0.00749    0.10000   0.09919
17530.49251    0.00749 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  6.29442E-001    3  2.60863E-001    4  2.90979E-002    5  7.49267E-001
6  2.60250E-003
   7  1.32050E-001    8  9.98264E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                        NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A        893.0982(207)          0.0000
   2        20000         B         685.617( 59)          -0.000
   3        30000         C        453.1270( 94)          0.0000
   4          200    -DeltaJ          -1.692(295)E-03        0.000E-03
   5         2000    -DeltaK        -0.01174( 88)          0.00000
   6         1100    -DeltaJK        0.01313(116)         -0.00000
   7        40100     -deltaJ          2.861(173)E-03        0.000E-03
   8        41000     -deltaK       -0.01926( 84)          0.00000
 MICROWAVE AVG =       -0.000187 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.023956 MHz, IR RMS =        0.00000
```

D2O_wuudu SPFIT Output

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  7  5  3  6  4  3              11070.57000  11070.53861    0.03139    0.10000   0.00000
   2:  7  5  3  6  4  3              11070.57000  11070.53861    0.03139    0.10000   0.00000
   3:  8  5  4  7  4  4              12422.21000  12422.23853   -0.02853    0.10000   0.00000
   4:  9  7  3  8  6  3              14511.28000  14511.33349   -0.05349    0.10000   0.00000
   5:  11  8  4 10  7  4              17479.59000  17479.56221    0.02779    0.10000   0.00000
   6:  13  2 11 12  2 10              13334.29000  13334.28483    0.00517    0.10000   0.00000
13334.28842    0.00158 0.5000
   7:  13  3 11 12  2 10              13334.29000  13334.29200   -0.00200    0.10000   0.00000
13334.28842    0.00158 0.5000
   8:  14  3 12 13  2 11              14232.16000  14232.05701    0.10299    0.10000   0.00000
   9:  15  3 12 14  3 11              15790.92000  15791.07577   -0.15577    0.10000   0.00000
15791.08205   -0.16205 0.5000
  10:  15  4 12 14  3 11              15790.92000  15791.08833   -0.16833    0.10000   0.00000
15791.08205   -0.16205 0.5000
  11:  16  4 12 15  4 11              17353.44000  17353.34249    0.09751    0.10000   0.00000
17353.38390    0.05610 0.5000
  12:  16  5 12 15  4 11              17353.44000  17353.42531    0.01469    0.10000   0.00000
17353.38390    0.05610 0.5000
  13:  17  0 17 16  0 16              15608.95000  15608.97472   -0.02472    0.10000   0.00000
15608.97472   -0.02472 0.5000
  14:  17  1 17 16  0 16              15608.95000  15608.97472   -0.02472    0.10000   0.00000
15608.97472   -0.02472 0.5000
  15:  18  1 17 17  1 16              17162.52000  17162.49467    0.02533    0.10000   0.00000
17162.49467    0.02533 0.5000
  16:  18  2 17 17  1 16              17162.52000  17162.49467    0.02533    0.10000   0.00000
17162.49467    0.02533 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  3.33326E-001   3  1.67519E-001   4  6.62688E-002   5  6.67432E-001
6  7.54276E-004
   7  1.17272E-001   8  9.99775E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A          884.948( 40)          -0.000
   2        20000          B          697.458( 60)           0.000
   3        30000          C          449.724( 38)          -0.000
   4          200    -DeltaJ            -6.67( 87)E-03        -0.00E-03
   5         2000     -DeltaK          -0.0253( 32)          -0.0000
   6         1100    -DeltaJK           0.0314( 41)           0.0000
   7        40100     -deltaJ           1.374(165)E-03       -0.000E-03
   8        41000     -deltaK          -0.0329( 33)          -0.0000
 MICROWAVE AVG =        0.000708 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.065843 MHz, IR RMS =        0.00000
```

D2O_wudud SPFIT Output

```
                   EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  6  6  1  5  5  1               10381.55000   10381.55628   -0.00628    0.10000   0.00000
   2:  6  6  1  5  5  1               10381.55000   10381.55628   -0.00628    0.10000   0.00000
   3:  7  5  2  6  4  2               10840.27000   10840.25856    0.01144    0.10000   0.00000
   4:  10  3  8  9  2  8               15241.84000   15241.85202   -0.01202    0.10000   0.00000
   5:  10 10  1  9  9  1                17501.95000   17501.94891    0.00109    0.10000   0.00000
   6:  11  2  9 10  2  8                11667.18000   11667.13430    0.04570    0.10000   0.00000
   7:  12  1 11 11  1 10                 11966.27000   11966.18021    0.08979    0.10000   0.00000
11966.18146    0.08854 0.5000
   8:  12  2 11 11  1 10                 11966.27000   11966.18271    0.08729    0.10000   0.00000
11966.18146    0.08854 0.5000
   9:  14  0 14 13  0 13                 13194.46000   13194.67774   -0.21774    0.10000   0.00000
13194.67774   -0.21774 0.5000
  10:  14  1 14 13  0 13                  13194.46000   13194.67774   -0.21774    0.10000   0.00000
13194.67774   -0.21774 0.5000
  11:  15  1 14 14  1 13                  14728.08000   14728.08803   -0.00803    0.10000   0.00000
14728.08804   -0.00804 0.5000
  12:  15  2 14 14  1 13                  14728.08000   14728.08805   -0.00805    0.10000   0.00000
14728.08804   -0.00804 0.5000
  13:  16  0 16 15  0 15                  15037.50000   15037.36128    0.13872    0.10000   0.00000
15037.36128    0.13872 0.5000
  14:  16  1 16 15  0 15                  15037.50000   15037.36128    0.13872    0.10000   0.00000
15037.36128    0.13872 0.5000
  15:  17  2 15 16  2 14                  17185.87000   17185.89998   -0.02998    0.10000   0.00000
17185.90000   -0.03000 0.5000
  16:  17  3 15 16  2 14                  17185.87000   17185.90002   -0.03002    0.10000   0.00000
17185.90000   -0.03000 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  7.96420E-001    3  2.35539E-001    4  3.43229E-002    5  5.97360E-001
6  1.69438E-003
   7  3.85199E-001    8  9.98626E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                   NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A        890.2716(151)         -0.0000
   2        20000          B         678.500( 81)           0.000
   3        30000          C        460.1564( 70)         -0.0000
   4          200    -DeltaJ           7.92( 58)E-03        -0.00E-03
   5         2000     -DeltaK         0.01910(157)         -0.00000
   6         1100   -DeltaJK        -0.02651(214)          0.00000
   7        40100     -deltaJ          4.154(293)E-03       -0.001E-03
   8        41000     -deltaK            8.92(121)E-03        -0.00E-03
 MICROWAVE AVG =        0.000466 MHz, IR AVG =         0.00000
 MICROWAVE RMS =        0.084154 MHz, IR RMS =        0.00000
```

D2O_wduud SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  6  1  5  5  1              10196.97000   10196.96408    0.00592    0.10000   0.00000
   2:   6  6  1  5  5  1              10196.97000   10196.96408    0.00592    0.10000   0.00000
   3:   7  6  1  6  5  1              11386.19000   11386.25401   -0.06401    0.10000   0.00000
   4:   9  4  5  8  3  5              14012.49000   14012.66948   -0.17948    0.10000   0.00000
   5:  10  4  7  9  3  7               15732.91000   15732.74497    0.16503    0.10000   0.00000
   6:  10  2  8  9  2  7               10537.67000   10537.73617   -0.06617    0.10000   0.00000
10537.76535   -0.09535 0.5000
   7:  10  3  8  9  2  7               10537.67000   10537.79453   -0.12453    0.10000   0.00000
10537.76535   -0.09535 0.5000
   8:  10 10  0  9  9  1               17158.17000   17158.19347   -0.02347    0.10000   0.00000
17158.16295    0.00705 0.5000
   9:  10 10  1  9  9  1               17158.17000   17158.13243    0.03757    0.10000   0.00000
17158.16295    0.00705 0.5000
  10:  11  1 10 10  1  9                10708.08000   10707.93947    0.14053    0.10000   0.00000
10707.93953    0.14047 0.5000
  11:  11  2 10 10  1  9                10708.08000   10707.93959    0.14041    0.10000   0.00000
10707.93953    0.14047 0.5000
  12:  11  6  5 10  5  5               16847.37000   16847.33163    0.03837    0.10000   0.00000
  13:  11  8  4 10  7  4               17476.25000   17476.24431    0.00569    0.10000   0.00000
  14:  13  0 13 12  0 12                11757.49000   11757.54124   -0.05124    0.10000   0.00000
11757.54124   -0.05124 0.5000
  15:  13  1 13 12  0 12                11757.49000   11757.54124   -0.05124    0.10000   0.00000
11757.54124   -0.05124 0.5000
  16:  12  2 10 11  2  9                12291.31000   12291.24261    0.06739    0.10000   0.00000
12291.24325    0.06675 0.5000
  17:  12  3 10 11  2  9                12291.31000   12291.24388    0.06612    0.10000   0.00000
12291.24325    0.06675 0.5000
  18:  14  4 10 13  4  9                15465.46000   15465.53382   -0.07382    0.10000   0.00000
  19:  17  1 17 16  1 16                15265.45000   15265.44391    0.00609    0.10000   0.00000
15265.44391    0.00609 0.5000
  20:  17  0 17 16  1 16                15265.45000   15265.44391    0.00609    0.10000   0.00000
15265.44391    0.00609 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  3.21935E-001    3  3.01146E-001    4  1.52053E-001    5  9.98102E-001
6  2.51728E-002
   7  9.23968E-001    8  8.39123E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                   NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A         870.1694( 96)         0.0000
   2        20000         B         725.4836(132)        -0.0000
   3        30000         C         438.7370( 66)        -0.0000
   4          200    -DeltaJ          1.577( 44)E-03        0.000E-03
   5         2000    -DeltaK          1.080(139)E-03        0.000E-03
```

```
  6      1100   -DeltaJK        -2.873(176)E-03     -0.000E-03
  7     40100    -deltaJ        0.1684(300)E-03     0.0000E-03
  8     41000    -deltaK         0.569(257)E-03      0.000E-03
MICROWAVE AVG =     -0.001614 MHz, IR AVG =      0.00000
MICROWAVE RMS =      0.087244 MHz, IR RMS =      0.00000
```

D2O_wuwdu SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   7  3  5  6  2  5              12530.46000   12530.47407   -0.01407    0.10000   0.09765
   2:   8  5  4  7  4  4              14973.30000   14973.30079   -0.00079    0.10000   0.09999
   3:  10  0 10  9  1  9               10598.68000   10598.67935    0.00065    0.10000   0.06692
   4:  10  1  9  9  1  8              11397.00000   11397.00143   -0.00143    0.10000   0.09996
   5:  10  1 10  9  1  9               10598.68000   10598.71048   -0.03048    0.10000   0.06693
   6:  10  4  7  9  3  7              17720.95000   17720.93813    0.01187    0.10000   0.09834
   7:  11  2 10 10  2  9               12412.62000   12412.56993    0.05007    0.10000   0.06425
   8:  11  3  8 10  4  7              13721.76000   13721.76894   -0.00894    0.10000   0.09906
   9:  14  3 11 13  4 10               17061.02000   17061.00504    0.01496    0.10000   0.09734
  10:  14  4 11 13  3 10               17108.54000   17108.56593   -0.02593    0.10000   0.09181
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  6.46371E-001    3  5.68982E-001    4  2.68956E-002    5  1.20171E-001
6  8.48027E-004
   7  1.39626E-001    8  9.78173E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                  NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1         10000          A          1153.38( 36)            -0.00
   2         20000          B          753.831(130)             0.000
   3         30000          C         510.3192(241)           -0.0000
   4           200    -DeltaJ         -0.0203( 33)            0.0000
   5          2000    -DeltaK          -0.0402( 65)             0.0000
   6          1100   -DeltaJK           0.0592( 97)            -0.0000
   7         40100     -deltaJ         0.01312(224)          -0.00000
   8         41000     -deltaK          -0.0351( 57)             0.0000
 MICROWAVE AVG =       -0.000410 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.021805 MHz, IR RMS =        0.00000
```

D2O_wwduu SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  5  2  5  4  2                 11938.32000   11938.32000    0.00000    0.10000   0.10000
   2:  11  0 11 10  1 10                   11772.76000   11772.70993    0.05007    0.10000   0.07071
   3:  11  1 11 10  1 10                   11772.66000   11772.71007   -0.05007    0.10000   0.07071
   4:  13  4  9 12  5  8                 17162.51000   17162.51000   -0.00000    0.10000   0.10000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  6.60643E-001    3  9.76639E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                  NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
  1        10000         A       1092.7203(141)         -0.0000
  2        20000         B        814.5854(195)          0.0000
  3        30000         C        516.2677( 37)         -0.0000
 MICROWAVE AVG =        0.000000 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.035407 MHz, IR RMS =        0.00000
```

D2O_wuwuu SPFIT Output

```
                     EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  2  5  5  1  5              10893.86000   10893.87163   -0.01163    0.10000   0.09941
   2:   9  3  6  8  2  6              15732.90000   15732.89499    0.00501    0.10000   0.09990
   3:  10  2  9  9  1  8              11357.45000   11357.48563   -0.03563    0.10000   0.09446
   4:  11  0 11 10  0 10              11546.44000   11546.44918   -0.00918    0.10000   0.09955
11546.45054   -0.01054 0.5000
   5:  11  1 11 10  0 10              11546.44000   11546.45189   -0.01189    0.10000   0.09955
11546.45054   -0.01054 0.5000
   6:  12  3  9 11  3  8              15091.55000   15091.51461    0.03539    0.10000   0.09444
   7:  13  3 11 12  2 10              15214.14000   15214.06358    0.07642    0.10000   0.07085
   8:  14  3 11 13  3 10              17062.51000   17062.56294   -0.05294    0.10000   0.08679
   9:  14  3 11 13  4 10              17049.37000   17049.38277   -0.01277    0.10000   0.10010
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  6.45859E-001    3  1.49703E-001    4  5.84292E-003    5  7.71266E-001
6  8.31505E-007
   7  9.49613E-002    8  3.59432E-001
MARQUARDT PARAMETER = 9.08602e-009, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1       10000        A        1139.53(107)          -0.01
   2       20000        B         770.44( 34)           0.00
   3       30000        C        506.478( 60)           0.000
   4         200    -DeltaJ      -0.0201(199)           0.0002
   5        2000    -DeltaK       -0.027( 44)           0.000
   6        1100    -DeltaJK       0.046( 64)          -0.000
   7       40100     -deltaJ       0.0152(123)         -0.0001
   8       41000     -deltaK      -0.025( 41)           0.000
 MICROWAVE AVG =      -0.000837 MHz, IR AVG =        0.00000
 MICROWAVE RMS =       0.038078 MHz, IR RMS =        0.00000
```

D2O_wwuud SPFIT Output

```
                      EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  7  3  4  6  2  4              12651.48000   12651.51809   -0.03809    0.10000   0.09503
   2:  7  4  4  6  3  4              13071.99000   13072.02354   -0.03354    0.10000   0.09617
   3:  8  8  0  7  7  1              16941.23000   16941.28234   -0.05234    0.10000   0.09999
16941.22798    0.00202 0.5000
   4:  8  8  1  7  7  1              16941.23000   16941.17363    0.05637    0.10000   0.09999
16941.22798    0.00202 0.5000
   5:  9  2  7  8  1  7              16789.62000   16789.56197    0.05803    0.10000   0.08804
   6:  9  4  6  8  3  5              12411.50000   12411.50616   -0.00616    0.10000   0.09987
   7:  10  1  9  9  1  8              11490.78000   11490.71651    0.06349    0.10000   0.09053
11490.72804    0.05196 0.5000
   8:  10  2  9  9  1  8              11490.78000   11490.73956    0.04044    0.10000   0.09053
11490.72804    0.05196 0.5000
   9:  11  8  4 10  8  3              15808.85000   15808.84232    0.00768    0.10000   0.09979
  10:  12  4  9 11  3  8              15265.42000   15265.49504   -0.07504    0.10000   0.07906
  11:  13  5  9 12  5  8              17151.97000   17151.94577    0.02423    0.10000   0.09789
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  1.08222E-001   3  5.53102E-001   4  1.55535E-001   5  2.12711E-001
6  1.29948E-002
   7  9.70338E-001   8  8.14517E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A         1083.029( 64)           0.000
   2        20000          B          831.529( 44)          -0.000
   3        30000          C         510.1725(277)           0.0000
   4          200    -DeltaJ           0.152(154)E-03        0.000E-03
   5         2000     -DeltaK            5.47( 90)E-03         0.00E-03
   6         1100    -DeltaJK          -5.50(108)E-03        -0.00E-03
   7        40100     -deltaJ          2.118(280)E-03        0.000E-03
   8        41000     -deltaK           1.90( 96)E-03         0.00E-03
 MICROWAVE AVG =       -0.000990 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.040773 MHz, IR RMS =        0.00000
```

D2O_wwdud SPFIT Output

```
                        EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   7  3  4  6  2  4              12562.03000   12562.07628   -0.04628    0.10000   0.09820
   2:   8  2  6  7  3  5              10670.29000   10670.08713    0.20287    0.10000   0.05674
   3:   9  1  9  8  0  8              10318.42000   10318.55124   -0.13124    0.10000   0.08463
   4:   9  8  2  8  7  2              17508.18000   17508.19305   -0.01305    0.10000   0.09986
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  9.38376E-001    3  9.93248E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                   NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A       1021.4800( 72)         -0.0000
   2        20000         B        838.8022( 76)          0.0000
   3        30000         C        552.9136( 50)          0.0000
 MICROWAVE AVG =        0.003076 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.123177 MHz, IR RMS =        0.00000
```

D2O_wwudu SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   8  2  7  7  1  7                14653.17000   14652.86267    0.30733    0.10000   0.07084
   2:   8  4  5  7  3  5                14550.80000   14551.06178   -0.26178    0.10000   0.06897
   3:  10  4  7  9  3  6                 13527.60000   13527.40895    0.19105    0.10000   0.06402
   4:  10  5  6  9  4  5                 14686.63000   14686.75974   -0.12974    0.10000   0.08627
   5:  12  5  7 11  6  6                  16855.37000   16855.45141   -0.08141    0.10000   0.09324
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  9.83032E-001    3  8.14042E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                 NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
  1        10000         A       1040.1180( 91)         -0.0000
  2        20000         B        826.1940( 43)          0.0000
  3        30000         C        540.7627( 58)          0.0000
 MICROWAVE AVG =        0.005091 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.211158 MHz, IR RMS =        0.00000
```

D2O_wuwud SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   9  2  7  8  1  7              15808.85000   15808.62664    0.22336    0.10000   0.08631
   2:  10  2  9  9  1  9              17888.73000   17888.92577   -0.19577    0.10000   0.08956
   3:  12  3  9 11  3  8              15053.12000   15052.89176    0.22824    0.10000   0.08556
   4:  12  4  9 11  4  8              14889.22000   14889.45241   -0.23241    0.10000   0.08499
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  3.18339E-001    3  9.58917E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A        1160.514( 44)          -0.000
   2        20000         B        744.3230(118)           0.0000
   3        30000         C        505.7563( 53)          0.0000
 MICROWAVE AVG =        0.005855 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.220408 MHz, IR RMS =        0.00000
```

D2O_wwwdu SPFIT Output

```
                          EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  6  4  3  5  3  2              11310.52000   11310.52073   -0.00073    0.10000   0.09723
   2:  7  5  3  6  5  2              13012.87000   13012.87167   -0.00167    0.10000   0.09405
   3:  7  6  2  6  6  1              13306.18000   13306.17961    0.00039    0.10000   0.09987
   4:  7  7  1  6  6  0              16279.02000   16279.01996    0.00004    0.10000   0.10000
   5:  8  3  5  7  3  4              13527.60000   13527.59011    0.00989    0.10000   0.05349
   6:  8  4  5  7  3  4              13529.70000   13529.70641   -0.00641    0.10000   0.05287
   7:  9  2  7  8  2  6              13739.83000   13739.83030   -0.00030    0.10000   0.07975
13739.83216   -0.00216 0.5000
   8:  9  3  7  8  2  6              13739.83000   13739.83403   -0.00403    0.10000   0.07975
13739.83216   -0.00216 0.5000
   9:  9  6  4  8  6  3              16667.62000   16667.61948    0.00052    0.10000   0.09886
  10:  17  5 12 17  4 13                12641.72000   12641.72025   -0.00025    0.10000   0.09974
12641.72025   -0.00025 0.5000
  11:  17  5 12 17  5 13                12641.72000   12641.72025   -0.00025    0.10000   0.09974
12641.72025   -0.00025 0.5000
  12:  18  7 12 18  6 13                12626.97000   12626.96990    0.00010    0.10000   0.09995
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  3.69807E-001    3  1.73616E-001    4  9.21532E-001    5  8.82758E-002
6  1.44566E-002
   7  9.69919E-001    8  2.81731E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A       1183.0933(253)          -0.0000
   2        20000         B       1081.6496(154)           0.0000
   3        30000         C          622.563( 32)          0.000
   4          200    -DeltaJ          -0.831(108)E-03       0.000E-03
   5         2000     -DeltaK            0.75( 43)E-03        0.00E-03
   6         1100   -DeltaJK           -1.63( 59)E-03       -0.00E-03
   7        40100     -deltaJ         -0.041(133)E-03      -0.000E-03
   8        41000     -deltaK            2.64(177)E-03        0.00E-03
 MICROWAVE AVG =       -0.000028 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.003840 MHz, IR RMS =        0.00000
```

D2O_wwwud SPFIT Output

```
                  EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  5  4  2  4  3  2             11306.15000   11306.16582   -0.01582    0.10000   0.09063
   2:  6  3  4  5  2  4             13492.19000   13492.22664   -0.03664    0.10000   0.06446
   3:  6  5  2  5  4  2             13588.95000   13588.92191    0.02809    0.10000   0.07647
   4:  7  3  4  6  2  4             15720.95000   15720.96541   -0.01541    0.10000   0.08588
   5:  7  3  5  6  2  5             15744.73000   15744.69388    0.03612    0.10000   0.08095
   6:  8  4  5  7  3  4             13607.72000   13607.71416    0.00584    0.10000   0.09883
   7:  8  7  2  7  7  1             15368.90000   15368.89917    0.00083    0.10000   0.09999
   8:  9  4  6  8  4  5             14866.67000   14866.66565    0.00435    0.10000   0.09499
   9:  9  6  4  8  5  3             17131.25000   17131.25493   -0.00493    0.10000   0.09926
  10:  10  5  6  9  5  5             17122.14000   17122.14627   -0.00627    0.10000   0.09598
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  9.70756E-001    3  7.31932E-001    4  1.64318E-001    5  1.39172E-001
6  1.68451E-002
   7  5.93207E-002    8  9.93737E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A         1173.543(108)          -0.000
   2        20000          B         1082.289( 91)           0.000
   3        30000          C          634.443( 42)           0.000
   4          200    -DeltaJ           -4.41( 60)E-03         0.00E-03
   5         2000     -DeltaK            -6.03(180)E-03         0.00E-03
   6         1100    -DeltaJK          0.01573(229)         -0.00000
   7        40100      -deltaJ            3.08(102)E-03        -0.00E-03
   8        41000      -deltaK          -0.0372( 53)           0.0000
 MICROWAVE AVG =       -0.000384 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.020103 MHz, IR RMS =        0.00000
```

D2O_wwuwd SPFIT Output

```
                            EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   5  3  2  4  2  2              11178.25000   11178.18122    0.06878    0.10000   0.04782
   2:   7  5  3  6  4  3              17693.38000   17693.41710   -0.03710    0.10000   0.08757
   3:   8  1  7  7  1  6              11013.60000   11013.60971   -0.00971    0.10000   0.04154
   4:   8  1  7  7  2  6              10720.68000   10720.68679   -0.00679    0.10000   0.08944
   5:  10  1  9  9  2  8               13231.82000   13231.81126    0.00874    0.10000   0.05428
   6:  11  0 11 10  0 10                13428.63000   13428.63357   -0.00357    0.10000   0.08583
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  5.97641E-001    3  9.82898E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                         NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
  1        10000         A       1560.5497(118)          -0.0000
  2        20000         B        850.2716(208)           0.0000
  3        30000         C        587.3559( 47)          -0.0000
 MICROWAVE AVG =        0.003391 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.032499 MHz, IR RMS =        0.00000
```

D2O_wwwdd SPFIT Output

```
                              EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  6  0  5  5  1                  14317.78000   14317.73173    0.04827    0.10000   0.09266
   2:   7  5  2  6  3  3                  17708.24000   17708.31046   -0.07046    0.10000   0.08359
   3:   8  3  5  7  4  4                  13409.81000   13409.86928   -0.05928    0.10000   0.08870
   4:   9  6  3  8  6  2                  17945.29000   17945.21469    0.07531    0.10000   0.08098
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  9.73228E-001    3  9.99177E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                        NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1         10000          A        1212.9260( 94)          0.0000
   2         20000          B        1076.7211( 44)         -0.0000
   3         30000          C         603.7366( 97)          0.0000
 MICROWAVE AVG =       -0.001538 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.064187 MHz, IR RMS =        0.00000
```

D2O_wwuwu SPFIT Output

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  5  3  3  4  2  3              11484.15000  11484.49164  -0.34164   0.10000  0.07150
   2:  5  4  2  4  3  2              12753.26000  12753.00837   0.25163   0.10000  0.08569
   3:  8  3  6  7  3  5              11645.70000  11645.84033  -0.14033   0.10000  0.09583
   4:  8  5  4  7  5  3              11943.55000  11943.35340   0.19660   0.10000  0.09156
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  4.46745E-001    3  9.92512E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000        A       1502.6606(133)        -0.0000
   2        20000        B        859.9598(165)        -0.0000
   3        30000        C        591.7598(201)         0.0000
 MICROWAVE AVG =       -0.008436 MHz, IR AVG =       0.00000
 MICROWAVE RMS =        0.244120 MHz, IR RMS =       0.00000
```

D2O_wwwwu SPFIT Output

```
                        EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  4  4  1  3  3  1              13209.81000   13209.81000   -0.00000    0.10000   0.10000
   2:  8  1  7  7  1  6              13466.53000   13466.58042   -0.05042    0.10000   0.07933
   3:  8  6  3  7  6  2              15467.91000   15467.91057   -0.00057    0.10000   0.10000
   4:  9  2  8  8  1  7              14886.66000   14886.59645    0.06355    0.10000   0.06412
   5:  10  0 10  9  1  9              14973.30000   14973.28674    0.01326    0.10000   0.09998
14973.29822    0.00178 0.5000
   6:  10  1 10  9  1  9              14973.30000   14973.30969   -0.00969    0.10000   0.09998
14973.29822    0.00178 0.5000
   7:  11  1 10 10  2  9              17730.48000   17730.49653   -0.01653    0.10000   0.09798
   8:  13  4  9 13  3 10              11265.24000   11265.23968    0.00032    0.10000   0.10000
   9:  14  3 11 14  2 12              14585.75000   14585.74897    0.00103    0.10000   0.09998
  10:  17  4 13 17  4 14              16985.83000   16985.83061   -0.00061    0.10000   0.10000
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  2.48725E-001   3  1.70831E-001   4  9.90207E-001   5  4.60502E-001
6  1.17002E-003
   7  1.12541E-001   8  8.12936E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A        1748.683(105)            0.000
   2        20000         B        1139.579( 45)           -0.000
   3        30000         C        715.9006(182)           -0.0000
   4          200    -DeltaJ           0.72(188)E-03        -0.00E-03
   5         2000    -DeltaK             1.6( 45)E-03         -0.0E-03
   6         1100    -DeltaJK           -4.1( 64)E-03          0.0E-03
   7        40100     -deltaJ          -0.66(113)E-03         0.00E-03
   8        41000     -deltaK             1.7( 39)E-03         -0.0E-03
 MICROWAVE AVG =       -0.000162 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.027609 MHz, IR RMS =        0.00000
```

D2O_wwwwd SPFIT Output

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   5  4  1  4  3  1              14866.67000   14866.66557    0.00443    0.10000   0.09987
   2:   6  2  5  5  1  5              16451.83000   16451.80194    0.02806    0.10000   0.09478
   3:   6  3  4  5  2  4              16512.95000   16513.00516   -0.05516    0.10000   0.07792
   4:   9  2  7  8  2  6              16497.45000   16497.39885    0.05115    0.10000   0.08137
   5:  10  3  8  9  3  7               17840.27000   17840.30199   -0.03199    0.10000   0.09317
   6:  11  3  8 11  3  9               10374.06000   10374.05779    0.00221    0.10000   0.09999
   7:  11  4  8 11  3  9               10517.87000   10517.85454    0.01546    0.10000   0.09843
   8:  16  4 13 16  2 14               17146.90000   17146.91083   -0.01083    0.10000   0.09993
17146.90336   -0.00336 0.5000
   9:  16  4 13 16  3 14               17146.90000   17146.89590    0.00410    0.10000   0.09993
17146.90336   -0.00336 0.5000
  10:  16  5 11 16  4 12               13739.83000   13739.83128   -0.00128    0.10000   0.09998
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  2.82814E-001   3  1.12323E-001   4  8.73705E-001   5  6.65377E-001
6  4.71991E-004
   7  3.89129E-002   8  9.99021E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1       10000         A        1723.002(284)           0.000
   2       20000         B        1158.257(133)          -0.000
   3       30000         C         728.868(109)          -0.000
   4         200    -DeltaJ          0.0107( 51)        -0.0000
   5        2000     -DeltaK          0.0238(119)         -0.0000
   6        1100    -DeltaJK         -0.0371(173)          0.0000
   7       40100     -deltaJ            -7.1( 32)E-03          0.0E-03
   8       41000     -deltaK          0.0203(104)         -0.0000
 MICROWAVE AVG =       0.001057 MHz, IR AVG =       0.00000
 MICROWAVE RMS =       0.029338 MHz, IR RMS =       0.00000
```

HDO1_wduud SPFIT Output

```
                           EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  6  1  5  5  1              10378.35000   10378.34958    0.00042    0.10000   0.10000
   2:   9  4  6  8  3  5              10518.43000   10518.43291   -0.00291    0.10000   0.09998
   3:  10  4  7  9  4  6              11347.28000   11347.20650    0.07350    0.10000   0.08494
   4:  10  5  6  9  4  6              15844.39000   15844.45962   -0.06962    0.10000   0.08661
   5:  11  3  8 10  4  7              12229.35000   12229.35199   -0.00199    0.10000   0.09999
   6:  11  4  7 10  3  7              17438.08000   17438.01068    0.06932    0.10000   0.08673
   7:  11  4  7 10  5  6              12937.53000   12937.59571   -0.06571    0.10000   0.08817
   8:  11  5  7 10  4  6              13005.76000   13005.76296   -0.00296    0.10000   0.09998
   9:  13  6  7 12  6  6              16395.73000   16395.73003   -0.00003    0.10000   0.10000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  2.67165E-002    3  1.64167E-001    4  1.91871E-001    5  7.95603E-001
6  6.16026E-003
   7  8.68043E-001    8  1.22055E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                        NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A          886.788(133)          0.000
   2        20000          B          729.407(159)         -0.000
   3        30000          C          441.763( 51)          0.000
   4          200    -DeltaJ            -0.23( 70)E-03        -0.00E-03
   5         2000     -DeltaK            1.33(220)E-03         0.00E-03
   6         1100    -DeltaJK           -0.38(259)E-03        -0.00E-03
   7        40100     -deltaJ            1.45( 88)E-03         0.00E-03
   8        41000     -deltaK           -8.40(242)E-03        -0.00E-03
 MICROWAVE AVG =        0.000002 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.046420 MHz, IR RMS =        0.00000
```

HDO1_wuduu SPFIT Output

```
                     EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   7  2  5  6  1  5              10748.19000   10748.20022   -0.01022    0.10000   0.09994
   2:   7  6  2  6  5  1              11770.65000   11770.57738    0.07262    0.10000   0.09696
   3:   7  7  0  6  6  1              12427.27000   12427.28201   -0.01201    0.10000   0.09992
   4:   8  6  3  7  5  2              12864.72000   12864.78078   -0.06078    0.10000   0.09788
   5:  10  3  7  9  3  6              11488.80000   11488.80172   -0.00172    0.10000   0.10000
   6:  14  4 11 13  3 10              15065.48000   15065.29303    0.18697    0.10000   0.07765
   7:  15  2 13 14  2 12              15319.69000   15319.89426   -0.20426    0.10000   0.07346
15319.89129   -0.20129 0.2500
   8:  15  2 13 14  3 12              15319.69000   15319.88667   -0.19667    0.10000   0.07346
15319.89129   -0.20129 0.2500
   9:  15  3 13 14  2 12              15319.69000   15319.89591   -0.20591    0.10000   0.07346
15319.89129   -0.20129 0.2500
  10:  15  3 13 14  3 12              15319.69000   15319.88832   -0.19832    0.10000   0.07346
15319.89129   -0.20129 0.2500
  11:  15  5 10 14  6  9              17277.23000   17277.25311   -0.02311    0.10000   0.09969
  12:  17  1 16 16  1 15              16492.74000   16492.68711    0.05289    0.10000   0.09840
16492.68711    0.05289 0.2500
  13:  17  1 16 16  2 15              16492.74000   16492.68711    0.05289    0.10000   0.09840
16492.68711    0.05289 0.2500
  14:  17  2 16 16  1 15              16492.74000   16492.68711    0.05289    0.10000   0.09840
16492.68711    0.05289 0.2500
  15:  17  2 16 16  2 15              16492.74000   16492.68711    0.05289    0.10000   0.09840
16492.68711    0.05289 0.2500
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  5.65989E-001    3  2.22021E-001    4  1.62530E-002    5  8.29973E-001
6  5.24002E-003
   7  9.95313E-001    8  1.37604E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                     NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A         910.567( 99)           0.000
   2        20000          B        688.5752(277)          -0.0000
   3        30000          C        456.6607(207)          -0.0000
   4          200    -DeltaJ           -1.33( 45)E-03        -0.00E-03
   5         2000     -DeltaK           -0.60( 50)E-03         0.00E-03
   6         1100    -DeltaJK            1.48( 87)E-03         0.00E-03
   7        40100     -deltaJ          0.616(313)E-03        0.000E-03
   8        41000     -deltaK           0.81( 49)E-03         0.00E-03
 MICROWAVE AVG =        0.000372 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.098897 MHz, IR RMS =        0.00000
```

HDO1_wdudu SPFIT Output

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   7  5  2  6  4  2                10968.19000   10967.90735    0.28265    0.10000   0.07727
   2:   9  4  5  8  3  5                13252.90000   13252.76131    0.13869    0.10000   0.06770
   3:  11  4  8 10  3  8                  16830.20000   16830.49077   -0.29077    0.10000   0.07212
   4:  13  5  8 12  6  7                  15244.43000   15244.28369    0.14631    0.10000   0.08113
   5:  14  6  9 13  6  8                  16497.45000   16497.58788   -0.13788    0.10000   0.08753
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  8.95165E-001    3  9.91106E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                        NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1         10000          A        900.6808( 87)           0.0000
   2         20000          B        684.1236( 32)          -0.0000
   3         30000          C        469.0249( 59)           0.0000
 MICROWAVE AVG =        0.027801 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.211705 MHz, IR RMS =        0.00000
```

HDO1_wudud SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  10  3  7  9  3  6                11558.26000   11557.89802    0.36198    0.10000   0.07905
   2:  14  3 11 13  3 10                 15180.98000   15180.51107    0.46893    0.10000   0.05131
   3:  14  5 10 13  4  9                 15844.39000   15844.92438   -0.53438    0.10000   0.06336
   4:  15  2 13 14  2 12                 15479.43000   15479.58633   -0.15633    0.10000   0.08864
   5:  15  6 10 14  6  9                 17369.22000   17369.24391   -0.02391    0.10000   0.09615
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  3.22828E-001    3  4.15294E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
  1         10000          A          908.057( 41)           0.000
  2         20000          B        680.4086(263)          -0.0000
  3         30000          C        464.2687( 62)           0.0000
 MICROWAVE AVG =        0.023260 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.363732 MHz, IR RMS =        0.00000
```

HDO1_wuudu SPFIT Output

```
                     EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  11  3  9 10  2  9              17201.05000   17202.15095   -1.10095    0.10000   0.09377
   2:  11  4  7 10  3  7              16977.39000   16977.28756    0.10244    0.10000   0.09682
   3:  11  5  7 10  5  6              12943.82000   12942.90852    0.91148    0.10000   0.03882
   4:  13  1 12 12  1 11               12776.11000   12777.14896   -1.03896    0.10000   0.05615
12777.14857   -1.03857 0.2500
   5:  13  1 12 12  2 11               12776.11000   12777.14800   -1.03800    0.10000   0.05615
12777.14857   -1.03857 0.2500
   6:  13  2 12 12  1 11               12776.11000   12777.14914   -1.03914    0.10000   0.05615
12777.14857   -1.03857 0.2500
   7:  13  2 12 12  2 11               12776.11000   12777.14818   -1.03818    0.10000   0.05615
12777.14857   -1.03857 0.2500
   8:  14  1 13 13  1 12               13681.55000   13683.03080   -1.48080    0.10000   0.06136
13683.03073   -1.48073 0.2500
   9:  14  1 13 13  2 12               13681.55000   13683.03062   -1.48062    0.10000   0.06136
13683.03073   -1.48073 0.2500
  10:  14  2 13 13  1 12                13681.55000   13683.03083   -1.48083    0.10000   0.06136
13683.03073   -1.48073 0.2500
  11:  14  2 13 13  2 12                13681.55000   13683.03065   -1.48065    0.10000   0.06136
13683.03073   -1.48073 0.2500
  12:  15  5 11 14  5 10                16606.61000   16604.25982    2.35018    0.10000   0.05905
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  3.08827E-001    3  9.45450E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000        A         902.591( 34)          -0.001
   2        20000        B        699.4352(119)           0.0005
   3        30000        C       452.99646(269)           0.00003
 MICROWAVE AVG =       -0.042691 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        1.344613 MHz, IR RMS =        0.00000
```

HDO1_wwdud SPFIT Output

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   7  5  3  6  4  3              13438.73000   13438.74566   -0.01566    0.10000   0.07125
   2:   8  1  7  7  0  7              15105.54000   15105.54324   -0.00324    0.10000   0.09894
   3:   9  6  4  8  5  4              17087.03000   17087.01444    0.01556    0.10000   0.07168
   4:  11  4  7 10  5  6               15861.09000   15861.09041   -0.00041    0.10000   0.09998
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  3.69874E-001    3  9.88347E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A       1065.7455(173)         -0.0000
   2        20000         B        855.9642(155)          0.0000
   3        30000         C        569.8553(133)         -0.0000
 MICROWAVE AVG =       -0.000937 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.011160 MHz, IR RMS =        0.00000
```

HDO1_wuwud SPFIT Output

```
                          EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   9  2  8  8  1  8                16455.31000   16455.29287    0.01713    0.10000   0.09926
   2:   9  6  4  8  6  3                11759.02000   11759.05190   -0.03190    0.10000   0.09741
   3:  12  3 10 11  3  9                  14401.81000   14401.70485    0.10515    0.10000   0.06668
   4:  13  3 10 12  3  9                  16365.20000   16365.28683   -0.08683    0.10000   0.07882
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  6.95698E-001    3  9.17561E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                     NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A        1217.6054(259)          -0.0000
   2        20000         B         751.8418( 67)           0.0000
   3        30000         C         514.6696( 40)          -0.0000
 MICROWAVE AVG =        0.000886 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.070548 MHz, IR RMS =        0.00000
```

HDO1_wwduu SPFIT Output

```
                              EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   8  1  7  7  0  7              15262.51000   15262.69215   -0.18215    0.10000   0.08658
   2:   8  5  4  7  4  4              15447.45000   15447.14852    0.30148    0.10000   0.05613
   3:   8  8  0  7  7  1              17867.76000   17867.86359   -0.10359    0.10000   0.09680
17867.85142   -0.09142 0.5000
   4:   8  8  1  7  7  1              17867.76000   17867.83924   -0.07924    0.10000   0.09680
17867.85142   -0.09142 0.5000
   5:  14  0 14 13  1 13                 15265.43000   15265.44594   -0.01594    0.10000   0.09990
15265.44595   -0.01595 0.5000
   6:  14  1 14 13  1 13                 15265.43000   15265.44595   -0.01595    0.10000   0.09990
15265.44595   -0.01595 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  8.53586E-001    3  9.99543E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                       NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1         10000          A        1144.2509( 67)          -0.0000
   2         20000          B          829.2658( 82)           0.0000
   3         30000          C          529.8739( 37)          -0.0000
 MICROWAVE AVG =        0.002991 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.182126 MHz, IR RMS =        0.00000
```

HDO1_wwudu SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   8  2  6  7  3  5              10813.32000   10812.93599    0.38401    0.10000   0.05089
   2:   9  1  8  8  1  7              11191.29000   11191.45277   -0.16277    0.10000   0.09311
   3:  10  5  6  9  4  5               15319.69000   15319.69245   -0.00245    0.10000   0.09999
   4:  10  5  6  9  5  5               14489.13000   14489.28827   -0.15827    0.10000   0.09348
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  9.58730E-001    3  4.56030E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                   NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
  1        10000         A       1085.7237(200)         -0.0000
  2        20000         B        841.0634(135)          0.0000
  3        30000         C        557.0169( 88)          0.0000
 MICROWAVE AVG =        0.015130 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.223055 MHz, IR RMS =        0.00000
```

HDO1_wuwdu SPFIT Output

```
                          EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  2  5  5  1  5              11035.70000   11035.20076    0.49924    0.10000   0.06971
   2:   8  4  5  7  3  5              14794.44000   14794.83965   -0.39965    0.10000   0.08189
   3:  12  4  9 11  3  8               15677.86000   15677.64379    0.21621    0.10000   0.09506
   4:  14  3 11 13  3 10                17471.55000   17471.72091   -0.17091    0.10000   0.09694
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  5.49425E-001    3  8.12874E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                     NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
  1        10000         A       1209.1670(251)          -0.0000
  2        20000         B        761.6147(121)           0.0000
  3        30000         C        519.5340( 51)           0.0000
 MICROWAVE AVG =        0.036222 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.348181 MHz, IR RMS =        0.00000
```

HDO1_wuwuu SPFIT Output

```
                        EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   7  2  5  6  1  5                12537.47000   12538.63399   -1.16399    0.10000   0.09201
   2:  10  4  7  9  4  6                 13145.21000  13142.66661    2.54339    0.10000   0.05175
   3:  14  1 14 13  1 13                 14886.66000  14887.62937   -0.96937    0.10000   0.09453
   4:  14  3 12 13  2 11                 16583.86000  16584.12534   -0.26534    0.10000   0.09960
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  3.52860E-001    3  8.45927E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A        1194.235(129)          -0.000
   2        20000          B        778.9241(155)          0.0000
   3        30000          C        516.6388( 43)          0.0000
 MICROWAVE AVG =        0.036173 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        1.486087 MHz, IR RMS =        0.00000
```

HDO1_wwdwd SPFIT Output

```
                              EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   8  3  6  7  2  6                17910.85000   17910.82839    0.02161    0.10000   0.08063
   2:  11  1 10 10  2  9                 15334.25000   15334.26571   -0.01571    0.10000   0.09027
   3:  13  3 11 13  2 12                 11151.15000   11151.17272   -0.02272    0.10000   0.07830
   4:  14  3 11 14  2 12                 10518.48000   10518.46979    0.01021    0.10000   0.09602
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  3.00783E-001    3  7.52088E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                        NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
  1        10000         A        1605.513( 34)          -0.000
  2        20000         B        895.2822( 81)          0.0000
  3        30000         C        627.6455( 44)          -0.0000
 MICROWAVE AVG =       -0.001656 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.018263 MHz, IR RMS =        0.00000
```

HDO1_wwwud SPFIT Output

```
                      EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   5  5  0  4  4  1            12322.81000   12322.81856   -0.00856    0.10000   0.09985
   2:   6  3  4  5  3  3            10628.52000   10628.53105   -0.01105    0.10000   0.09975
   3:   7  3  5  6  2  4            11972.55000   11972.42413    0.12587    0.10000   0.06124
   4:   8  2  6  7  2  5            13306.15000   13306.23989   -0.08989    0.10000   0.07954
13306.24650   -0.09650 0.5000
   5:   8  3  6  7  2  5            13306.15000   13306.25311   -0.10311    0.10000   0.07954
13306.24650   -0.09650 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  1.09172E-001    3  8.69464E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                        NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
  1        10000          A         1235.389(100)           0.000
  2        20000          B         1150.776(145)          -0.000
  3        30000          C         667.9763(191)           0.0000
 MICROWAVE AVG =        0.002440 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.079608 MHz, IR RMS =        0.00000
```

HDO2_wwwwu SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   8  2  6  7  2  5                16267.10000   16267.08586    0.01414    0.10000   0.09817
   2:   9  1  8  8  2  7                15974.20000   15974.27427   -0.07427    0.10000   0.05420
   3:   9  1  9  8  1  8                14550.80000   14550.79369    0.00631    0.10000   0.05499
   4:   9  3  7  8  3  6                17331.00000   17330.94460    0.05540    0.10000   0.06790
   5:  14  4 11 14  2 12                  15666.59000   15666.59609   -0.00609    0.10000   0.09895
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  1.92701E-001    3  9.10797E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                   NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1         10000          A         1975.782( 89)          -0.000
   2         20000          B       1199.1085(221)           0.0000
   3         30000          C        768.2722( 33)          0.0000
 MICROWAVE AVG =       -0.000904 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.042099 MHz, IR RMS =        0.00000
```

HDO2_wwwwd SPFIT Output

```
                          EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  1  5  5  1  4              11711.55000   11710.43678    1.11322    0.10000   0.04308
   2:   6  3  4  5  2  3              14951.57000   14951.72668   -0.15668    0.10000   0.09919
   3:   7  1  7  6  1  6              11673.86000   11674.11715   -0.25715    0.10000   0.09780
   4:   9  3  7  8  3  6              17573.40000   17573.83714   -0.43714    0.10000   0.09355
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  9.94376E-001    3  4.95432E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                     NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A        1945.3595(290)          0.0000
   2        20000         B        1218.3171(275)          0.0001
   3        30000         C         783.1562( 94)         -0.0000
 MICROWAVE AVG =        0.065561 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.616652 MHz, IR RMS =        0.00000
```

HDO1_wwwwd SPFIT Output

```
                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   4  4  0  3  3  1              14491.76000   14491.22850    0.53150    0.10000   0.09618
   2:   8  2  6  7  3  5              15569.14000   15567.84499    1.29501    0.10000   0.07450
   3:  10  1  9  9  2  8               17840.27000   17841.51817   -1.24817    0.10000   0.07660
   4:  11  3  8 11  2  9                11087.17000   11087.67312   -0.50312    0.10000   0.09655
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  8.55651E-001    3  9.85012E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                   NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A       1919.0414(140)          0.0000
   2        20000         B       1233.9826( 53)          0.0000
   3        30000         C        784.9006( 41)          0.0000
 MICROWAVE AVG =        0.018806 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.970902 MHz, IR RMS =        0.00000
```

Appendix D

SUPPLEMENTARY INFORMATION FOR CHAPTER 5

Supplementary Information for Cooperativity in Methanol and Water Pentamers and Hexamers
S.E. Dutton, E.M. Mastin, G.A. Blake

SPFIT File for Asymmetric MeOH Hexamer

```
                          EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  11  7  5 10  5  6              11450.09000   11450.09041   -0.00041    0.10000  0.07071
   2:  13  6  8 12  5  8              11553.57000  11553.56960   0.00040    0.10000   0.09998
   3:  18  6 12 17  6 11               12414.44000  12414.45840   -0.01840    0.10000   0.09609
   4:  19  1 18 18  2 17               11386.97000  11386.99502  -0.02502    0.10000   0.09593
   5:  19  5 14 18  5 13               12665.57000  12665.50759   0.06241    0.10000   0.07213
   6:  21  2 19 20  3 18               12854.50000  12854.47578   0.02422    0.10000   0.09409
   7:  22  6 16 21  7 15               14707.50000  14707.53127  -0.03127    0.10000   0.05639
   8:  23  6 17 22  7 16               15281.20000  15281.23550  -0.03550    0.10000   0.06991
   9:  25  8 17 24  9 16               17071.23000  17071.20819   0.02181    0.10000  0.09702
  10:  26  3 23 25  3 22                16044.27000  16044.26710    0.00290    0.10000   0.10037
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  4.87819E-002   3  9.23875E-001    4  2.96087E-003    5  3.37345E-001
6  1.14464E-003
   7  8.07189E-002    8  3.98702E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                         NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1         10000          A          477.32( 53)          -0.00
   2         20000          B         420.781(271)           0.000
   3         30000          C         287.030( 66)          0.000
   4           200     -DeltaJ          0.121(265)E-03        0.000E-03
   5          2000     -DeltaK            1.76(115)E-03        -0.00E-03
   6          1100    -DeltaJK          -1.83( 99)E-03         0.00E-03
   7         40100     -deltaJ          -0.08( 64)E-03       -0.00E-03
   8         41000     -deltaK            5.4( 35)E-03        -0.0E-03
 MICROWAVE AVG =        0.000066 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.027251 MHz, IR RMS =        0.00000
```

SPFIT File for Prism 3M

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  7  4  4  6  3  4              11452.89000  11452.90482   -0.01482    0.10000   0.00000
   2:  7  7  1  6  6  1              14066.24000  14066.23791    0.00209    0.10000   0.00000
   3:  10  0 10  9  0  9              11190.55000  11190.71201   -0.16201    0.10000   0.00000
11190.71201   -0.16201 0.5000
   4:  10  0 10  9  0  9              11190.55000  11190.71201   -0.16201    0.10000   0.00000
11190.71201   -0.16201 0.5000
   5:  10  1  9  9  1  8             11648.91000  11648.76684    0.14316    0.10000   0.00000
   6:  10  5  6  9  5  5             12000.00000  12000.00023   -0.00023    0.10000   0.00000
   7:  11  0 11 10  0 10              12288.12000  12287.52126    0.59874    0.10000   0.00000
12288.10979    0.01021 0.5000
   8:  11  1 11 10  0 10              12288.12000  12288.69831   -0.57831    0.10000   0.00000
12288.10979    0.01021 0.5000
   9:  12  0 12 11  0 11              13385.09000  13384.75041    0.33959    0.10000   0.00000
13385.02687    0.06313 0.5000
  10:  12  1 12 11  0 11              13385.09000  13385.30334   -0.21334    0.10000   0.00000
13385.02687    0.06313 0.5000
  12:  12  1 11 11  2 10              13781.06000  13781.03057    0.02943    0.10000   0.00000
  13:  13  1 12 12  1 11              14912.56000  14912.53449    0.02551    0.10000   0.00000
  14:  13  1 12 12  2 11              14891.43000  14891.51118   -0.08118    0.10000   0.00000
  15:  14  1 13 13  1 12              16006.57000  16006.60377   -0.03377    0.10000   0.00000
  16:  16  0 16 15  0 15              17775.03000  17775.01415    0.01585    0.10000   0.00000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  8.62121E-001    3  2.50865E-001    4  1.40142E-002    5  5.98298E-001
6  1.25150E-003
   7  7.76503E-002    8  9.99142E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A        1032.834(114)           0.000
   2        20000          B         641.79( 60)           -0.00
   3        30000          C        548.8316(299)          0.0000
   4          200    -DeltaJ           9.77(174)E-03        0.00E-03
   5         2000    -DeltaK        -0.01217(184)          0.00000
   6         1100    -DeltaJK          2.4( 35)E-03        -0.0E-03
   7        40100     -deltaJ       -0.01204(155)          0.00000
   8        41000     -deltaK          -3.47(214)E-03       -0.00E-03
 MICROWAVE AVG =       -0.000221 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.071037 MHz, IR RMS =        0.00000
```

SPFIT File for Singly Deuterated Prism 3M

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   8  5  4  7  4  4              13428.65000   13428.65083   -0.00083    0.10000   0.00000
   2:   8  7  2  7  6  2              15178.09000   15178.08860    0.00140    0.10000   0.00000
   3:   9  8  2  8  7  2              17240.19000   17240.19075   -0.00075    0.10000   0.00000
   4:  12  2 11 11  2 10                 13746.74000   13746.72923    0.01077    0.10000   0.00000
   5:  13  1 12 12  1 11                 14855.23000   14855.27213   -0.04213    0.10000   0.00000
   6:  13  2 11 12  2 10                 15343.56000   15343.55856    0.00144    0.10000   0.00000
   7:  14  1 13 13  1 12                 15948.17000   15944.98054    3.18946    0.10000   0.00000
15948.12216    0.04784 0.5000
   8:  14  2 13 13  1 12                 15948.17000   15951.26378   -3.09378    0.10000   0.00000
15948.12216    0.04784 0.5000
   9:  15  1 15 14  0 14                 16610.89000   16610.88944    0.00056    0.10000   0.00000
  10:  15  2 14 14  1 13                  17037.51000   17039.10816   -1.59816    0.10000   0.00000
17037.52835   -0.01835 0.5000
  11:  15  1 14 14  1 13                  17037.51000   17035.94854    1.56146    0.10000   0.00000
17037.52835   -0.01835 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  3.45073E-001    3  7.79551E-002    4  2.39972E-002    5  5.33902E-001
6  3.01292E-003
   7  1.20724E-001    8  9.99123E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                          NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A         1030.233( 50)           0.000
   2        20000          B          635.661(129)           0.000
   3        30000          C          547.195( 36)          -0.000
   4          200    -DeltaJ          -4.199(238)E-03        0.000E-03
   5         2000    -DeltaK         -0.02341(146)          0.00000
   6         1100    -DeltaJK         0.02627(156)         -0.00000
   7        40100     -deltaJ         -2.166(102)E-03        0.000E-03
   8        41000     -deltaK          -7.02( 84)E-03        0.00E-03
 MICROWAVE AVG =       -0.000006 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.022415 MHz, IR RMS =        0.00000
```

SPFIT File for Cage 3M

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  5  2  5  4  2             13514.95000   13514.96522   -0.01522    0.10000   0.00000
   2:   7  5  3  6  4  3             14489.21000   14489.19396    0.01604    0.10000   0.00000
   3:   7  7  1  6  6  1             17896.34000   17896.34017   -0.00017    0.10000   0.00000
   4:  11   2 10 10  2  9             10560.84000   10560.78669    0.05331    0.10000   0.00000
   5:  12   0 12 11  0 11             11067.91000   11067.58644    0.32356    0.10000   0.00000
   6:  13   0 13 12  0 12             11964.16000   11964.39235   -0.23235    0.10000   0.00000
   7:  13   2 12 12  2 11             12412.75000   12412.73474    0.01526    0.10000   0.00000
   8:  15   1 15 14  0 14             13767.72000   13767.73764   -0.01764    0.10000   0.00000
   9:  15   2 14 14  2 13             14244.19000   14244.38075   -0.19075    0.10000   0.00000
  10:  16   1 16 15  0 15             14664.18000   14664.22491   -0.04491    0.10000   0.00000
  11:  18   1 17 17  2 16             16913.79000   16913.72170    0.06830    0.10000   0.00000
  12:  18   2 17 17  1 16             17046.86000   17046.82660    0.03340    0.10000   0.00000
  13:  20   0 20 19  0 19             18259.70000   18259.40704    0.29296    0.10000   0.00000
18259.68263    0.01737 0.5000
  14:  20   1 20 19  0 19             18259.70000   18259.95823   -0.25823    0.10000   0.00000
18259.68263    0.01737 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000   2  6.03114E-001    3  2.68454E-001    4  6.33378E-003    5  5.55086E-001
6  5.51034E-003
   7  9.03309E-002    8  9.99844E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                         NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A        1339.128( 47)          0.000
   2        20000          B         524.722( 36)          0.000
   3        30000          C        449.9792( 54)          0.0000
   4          200    -DeltaJ          -0.663(300)E-03      -0.000E-03
   5         2000    -DeltaK            5.98( 42)E-03        0.00E-03
   6         1100    -DeltaJK          -5.23( 39)E-03       -0.00E-03
   7        40100     -deltaJ         -0.559(106)E-03       0.000E-03
   8        41000     -deltaK           4.50( 36)E-03        0.00E-03
 MICROWAVE AVG =        0.002014 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.126199 MHz, IR RMS =        0.00000
```

SPFIT File for Singly Deuterated Cage 3M

```
                          EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  5  4  2  4  3  2              10783.45000   10783.44595    0.00405    0.10000   0.00000
   2:  5  5  1  4  4  1              12477.04000   12477.04686   -0.00686    0.10000   0.00000
   3:  6  6  1  5  5  1              15138.98000   15138.97628    0.00372    0.10000   0.00000
   4:  11  1 11 10  0 10               10196.99000   10196.88639    0.10361    0.10000   0.00000
   5:  12  2 11 11  2 10               11453.78000   11453.66527    0.11473    0.10000   0.00000
   6:  14  1 13 13  2 12               13021.75000   13021.72454    0.02546    0.10000   0.00000
   7:  14  2 13 13  2 12               13291.92000   13292.11269   -0.19269    0.10000   0.00000
   8:  15  0 15 14  0 14               13728.44000   13728.50413   -0.06413    0.10000   0.00000
   9:  15  1 14 14  1 13               14289.16000   14289.18828   -0.02828    0.10000   0.00000
  10:  19  1 18 18  1 17                17840.28000   17840.21670    0.06330    0.10000   0.00000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  7.07193E-001    3  4.50022E-001    4  7.16892E-003    5  2.31410E-001
6  2.55612E-003
   7  5.14058E-002    8  9.99839E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A         1332.962( 45)           0.000
   2        20000          B          521.256( 55)           0.000
   3        30000          C         449.2600( 78)           0.0000
   4          200     -DeltaJ          4.60( 42)E-03        -0.00E-03
   5         2000     -DeltaK         -0.01775(156)          0.00000
   6         1100    -DeltaJK        0.01360(134)         -0.00000
   7        40100      -deltaJ         - 2.889(145)E-03        0.000E-03
   8        41000      -deltaK         -0.01095(125)          0.00000
 MICROWAVE AVG =        0.002291 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.084066 MHz, IR RMS =        0.00000
```

SPFIT File for Cage 4M

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   6  6  1  5  5  1              10630.74000   10630.76572   -0.02572    0.10000   0.00000
   2:   7  6  2  6  5  2              11555.67000   11555.65721    0.01279    0.10000   0.00000
   3:   7  7  1  6  6  1              12478.51000   12478.48969    0.02031    0.10000   0.00000
   4:   9  8  2  8  7  2              15252.50000   15252.50803   -0.00803    0.10000   0.00000
   5:  13  0 13 12  0 12                 10458.16000   10458.30371   -0.14371    0.10000   0.00000
   6:  14  0 14 13  0 13                 11242.40000   11242.40434   -0.00434    0.10000   0.00000
11242.41138   -0.01138 0.5000
   7:  14  1 14 13  0 13                 11242.40000   11242.41842   -0.01842    0.10000   0.00000
11242.41138   -0.01138 0.5000
   8:  14  2 12 13  2 11                 12331.86000   12331.86096   -0.00096    0.10000   0.00000
   9:  15  1 14 14  1 13                 12558.67000   12558.63671    0.03329    0.10000   0.00000
  10:  15  1 15 14  0 14                  12026.67000   12026.52178    0.14822    0.10000   0.00000
  11:  17  1 16 16  1 15                  14126.49000   14126.49077   -0.00077    0.10000   0.00000
14126.51675   -0.02675 0.5000
  12:  17  2 16 16  1 15                  14126.49000   14126.54273   -0.05273    0.10000   0.00000
14126.51675   -0.02675 0.5000
  13:  18  0 18 17  0 17                  14378.72000   14378.83233   -0.11233    0.10000   0.00000
14378.83246   -0.11246 0.5000
  14:  18  1 18 17  0 17                  14378.72000   14378.83259   -0.11259    0.10000   0.00000
14378.83246   -0.11246 0.5000
  15:  20  0 20 19  0 19                  15947.07000   15946.98791    0.08209    0.10000   0.00000
15946.98793    0.08207 0.5000
  16:  20  1 20 19  0 19                  15947.07000   15946.98794    0.08206    0.10000   0.00000
15946.98793    0.08207 0.5000
  17:  21  0 21 20  0 20                  16731.27000   16731.04274    0.22726    0.10000   0.00000
16731.04274    0.22726 0.5000
  18:  21  1 21 20  0 20                  16731.27000   16731.04275    0.22725    0.10000   0.00000
16731.04274    0.22726 0.5000
  19:  22  0 22 21  0 21                  17514.87000   17515.08007   -0.21007    0.10000   0.00000
17515.08007   -0.21007 0.5000
  20:  22  1 22 21  0 21                  17514.87000   17515.08008   -0.21008    0.10000   0.00000
17515.08007   -0.21007 0.5000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  2.62346E-001    3  2.13928E-001    4  6.21638E-003    5  6.12598E-001
6  1.04980E-003
   7  1.26456E-001    8  9.99926E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                      NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000          A          924.664( 33)           0.000
   2        20000          B          522.129(264)          -0.000
   3        30000          C        392.0856( 85)           0.0000
   4          200    -DeltaJ           -1.540(248)E-03       -0.000E-03
```

```
  5        2000    -DeltaK          5.57(123)E-03       -0.00E-03
  6        1100   -DeltaJK         -4.00(133)E-03        0.00E-03
  7       40100    -deltaJ        -3.080(234)E-03       0.000E-03
  8       41000    -deltaK          8.84( 99)E-03       -0.00E-03
MICROWAVE AVG =      -0.001081 MHz, IR AVG =       0.00000
MICROWAVE RMS =       0.107250 MHz, IR RMS =       0.00000
```

SPFIT File for Singly Deuterated Cage 4M

```
                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:  6  6  1  5  5  1              10592.33000   10592.33000    0.00000    0.10000   0.00000
   2:  10  9  2  9  8  2              17037.51000   17037.51000   -0.00000    0.10000   0.00000
   3:  15  1 14 14  1 13               12530.46000   12530.25454    0.20546    0.10000   0.00000
12530.46066   -0.00066 0.5000
   4:  15  2 14 14  1 13               12530.46000   12530.66679   -0.20679    0.10000   0.00000
12530.46066   -0.00066 0.5000
   5:  16  0 16 15  0 15               12784.90000   12784.89301    0.00699    0.10000   0.00000
12784.89394    0.00606 0.5000
   6:  16  1 16 15  0 15               12784.90000   12784.89487    0.00513    0.10000   0.00000
12784.89394    0.00606 0.5000
   7:  18  1 18 17  0 17               14350.89000   14350.89772   -0.00772    0.10000   0.00000
14350.89761   -0.00761 0.5000
   8:  18  0 18 17  0 17               14350.89000   14350.89749   -0.00749    0.10000   0.00000
14350.89761   -0.00761 0.5000
   9:  20  2 18 19  2 17               16970.34000   16970.23376    0.10624    0.10000   0.00000
16970.33999    0.00001 0.5000
  10:  20  3 18 19  2 17               16970.34000   16970.44621   -0.10621    0.10000   0.00000
16970.33999    0.00001 0.5000
  11:  21  2 20 20  1 19               17226.74000   17226.73808    0.00192    0.10000   0.00000
17226.73740    0.00260 0.5000
  12:  21  1 20 20  1 19               17226.74000   17226.73672    0.00328    0.10000   0.00000
17226.73740    0.00260 0.5000
  13:  22  0 22 21  0 21               17479.56000   17479.55816    0.00184    0.10000   0.00000
17479.55816    0.00184 0.5000
  14:  22  1 22 21  0 21               17479.56000   17479.55816    0.00184    0.10000   0.00000
17479.55816    0.00184 0.5000
  15:  22  2 21 21  1 20               18006.15000   18006.15206   -0.00206    0.10000   0.00000
NORMALIZED DIAGONAL:
   1  1.00000E+000    2  2.76281E-001    3  1.41496E-001    4  2.13265E-003    5  6.18307E-001
6  3.39805E-003
   7  1.18741E-001    8  9.98166E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                    NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1        10000         A         919.809( 41)          0.000
   2        20000         B         518.953(146)         -0.000
   3        30000         C        391.1066(181)          0.0000
   4          200    -DeltaJ          -0.15( 56)E-03        0.00E-03
   5         2000    -DeltaK         0.06824( 57)        -0.00000
   6         1100   -DeltaJK        -0.06783( 42)        -0.00000
   7        40100     -deltaJ       -0.01826( 77)         0.00000
   8        41000     -deltaK        0.09166(226)        -0.00000
 MICROWAVE AVG =        0.000020 MHz, IR AVG =        0.00000
```

```
MICROWAVE RMS =        0.003487 MHz, IR RMS =        0.00000
```