MOLECULAR STRUCTURES OF DEUTERATED ISOTOPOLOGUES OF 2-AMINOPYRIDINE AND MICROWAVE SPECTROMETER DEVELOPMENT

By

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Abstract

This project had two main goals: develop a program to run a microwave spectrometer and use the technique of microwave spectroscopy to determine the molecular structure of three deuterated isotopologues of 2-aminopyridine. The first goal was achieved by using LabVIEW 2019 SP1 software to develop a program that allows for manual and automated measurements of rotational transitions. To achieve the second goal, the isotopologues of 2-aminopyridine were first synthesized via deuterium substitution of the parent molecule. High-level calculations using ab initio and density functional theory (DFT) methods and various basis sets were performed to predict rotational constants, quadrupole coupling constants, and frequencies of rotational transitions. Transitions were measured in the region of 4.4-10.9 GHz for each of the isotopologues of 2-aminopyridine, with both a and b-type transitions detected for two isotopologues. Measured rotational transitions were fit to a rigid asymmetric rotor for the isotopologues to determine experimental values of rotational constants of the molecule and quadrupole coupling constants for the ^{14}N and ^{2}H atoms within each isotopologue. The findings of this molecular study will be used to investigate the rotational structure of hydrogen-bonded complexes of 2-aminopyridine with small organic molecules. The spectrometer program will be used to measure rotational transitions for various other molecules and complexes.

Rotational Structure of Deuterated Isotopologues of 2-aminopyridine

Abstract:

Our lab uses high-resolution microwave spectroscopy to measure rotational spectra and structures of small molecules. Analogs of DNA bases, like 2-aminopyridine, can be investigated with ease in isolated systems. The analysis of 2-aminopyridine can provide insight into the structures of DNA bases, which are difficult to examine in biological environments. The purpose of this project was to use microwave spectroscopy to determine the structures of three isotopologues of 2-aminopyridine with varying degrees of deuteration of its amino group. Calculations were performed using ab initio methods (Møller-Plesset Perturbation Theory (MP2)) and density functional theory (DFT) methods (Minnesota 11 (M11) and B3LYP) with various basis sets to predict rotational transitions for each isotopologue. These transitions were used to determine the rotational constants and quadrupole coupling constants for the ^{14}N and ^{2}H atoms in the isotopologues. These findings can be used in the future analysis of complexes containing 2-aminopyridine, such as the heterodimer of 2-aminopyridine and formic acid.

Introduction:

2-aminopyridine is a small organic molecule that can serve as a structural analog for the nucleic acid base adenine. This molecule can undergo hydrogen-bonding with other small molecules such as 2-pyridone and imitate adenine base-pairing with uracil as studied in the paper by Leutwyler, et al[1]. 2-aminopyridine is also commonly used in the pharmaceutical industry to synthesize various pharmacophores[2], making it an interesting molecule to study.

The technique of microwave spectroscopy is particularly useful for determining the structure of small, gaseous molecules in addition to inorganic compounds[3] and hydrogen-bonded complexes[4]. The basis of this spectroscopic tool is that molecules have quantized rotational states, and the energy difference between two rotational states can be transferred to a molecule using light in the microwave frequency range. When the molecule absorbs this light, a rotation of the molecule is induced. The frequencies of microwave light that a molecule absorbs can be assigned to specific rotational transitions defined by quantum states with specific rotational quantum numbers associated with these states (J, K_a, K_c, etc.). These rotational transitions for a molecule can then be “fit” to a rotational model, which predicts the frequencies of rotational transitions based on properties of a molecule called rotational constants. The rotational constants usually of interest are A, B, and C, and these values are related to the moments of inertia of a molecule based on the principle axis basis set. The rotational model for 2-aminopyridine and its isotopologues is referred to as a rigid asymmetric rotor. The “rigid” term means that a molecule is treated as having fixed bond lengths and angles as it rotations. The “asymmetric” term means that the moments of inertia of the molecule are different along each of the principle axes. “Rotor” indicates that the molecule is rotating.

The parent isotopologue of 2-aminopyridine has been studied extensively using microwave spectroscopy by Kydd and Mills[5] and our group[6]. In the Kydd and Mills paper, researchers analyzed rotational transitions of 2-aminopyridine in the frequency range of 27-37 GHz. With their experimental setup and instrument, they were unable to assign quadrupole splitting due to the ^{14}N atoms within the molecule. Our group was able to measure the quadrupolar signatures for this molecule in the region of 4.5-13.2 GHz. This allowed for the determination of quadrupole coupling constants due to the ^{14}N atoms. Kydd and Mills analyzed different deuterated isotopologues of 2-aminopyridine, but they were unable to measure quadrupolar signals due to their low resolution. Therefore, the main purpose of this paper was to determine the quadrupolar coupling constants for three deuterated isotopologues of 2-aminopyridine (Figure 1).

The phenomenon of quadrupole splitting comes about when a nucleus has a spin quantum number greater than ½. ^{14}N and ^{2}H are atoms with spin quantum numbers of 1, so they will experience quadrupole splitting. Quadrupole splitting essentially means that rotational energy levels are split into different energy levels. Measuring the energy of transitions between quadrupolar rotational states can be used to determine quadrupolar coupling constants, which describe the local electronic environment for an atom within a molecule. For the deuterated isotopologues of 2-aminopyridine, there are multiple quadrupolar atoms that introduce extensive signal splitting. Once the values of quadrupole coupling constants for these isotopologues are experimentally determined, they can be compared to computational predictions of these values to assess the efficacy of different methods and basis sets in modeling quadrupolar molecules. For future work, hydrogen-bonded complexes of 2-aminopyridine with small organic molecules like formic acid can be formed. If deuterated isotopologues of 2-aminopyridine are used in these complexes, the quadrupole coupling constants of the 2-aminopyridine monomer can be compared to the quadrupole coupling constants in the complex as a way to measure the change in the local electronic environment of the molecule.

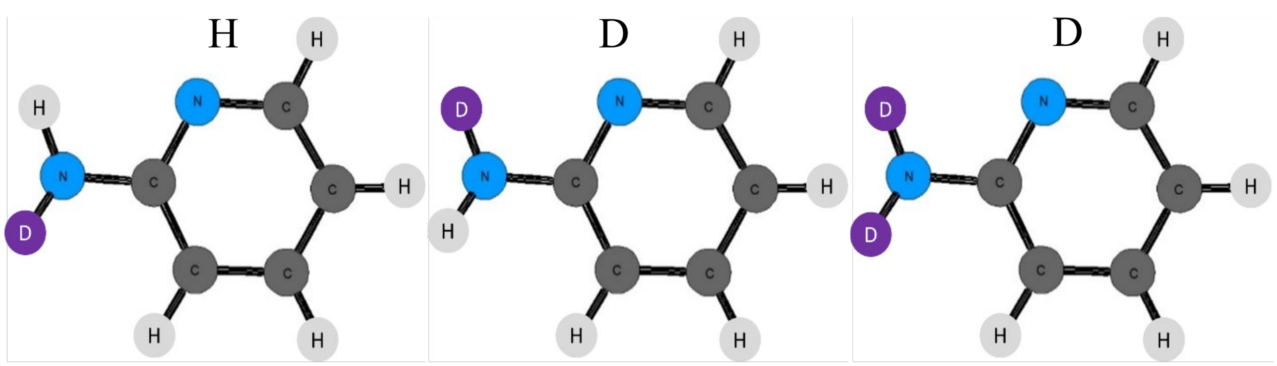

Figure 1: Deuterated isotopologues of 2-aminopyridine. The term "HD isotopologue," "DD Isotopologue," and "DH Isotopologue" are introduced here and will be used in the rest of this paper.

In the work by Kydd and Mills[5], two vibrational states of 2-aminopyridine were studied which described the inversion of the amino group of the molecule, and the two vibrational states were labeled by the terms 0^- and 0^+. Kydd and Mills were able to detect rotational transitions for both vibrational states, but our group was only able to detect transitions for the 0^+ vibrational state[6]. It was hypothesized that the excited 0^- was not detected because our instrument uses supersonic expansion when introducing molecules to its cavity, so the temperature of these molecules would likely be near the range of a few kelvin. As a result, there was likely insufficient population of the excited 0^- state which would explain the inability to detect transitions for this vibrational state. The inability to detect transitions for the 0^- state also occurred for the deuterated isotopologues of 2-aminopyridine, and the reason for this is most likely the same reason that the 0^- was not detected for the parent isotopologue.

Experimental:

Rotational transitions were measured for the 0^+ vibrational state of three deuterated isotopologues of 2-aminopyridine in the region of 4.4-10.9 GHz using a Flygare-Balle type pulsed-beam Fourier transform microwave spectrometer that was previously described by our group[4]. The parent molecule, 2-aminopyridine (98%), was purchased from Sigma-Aldrich, and the deuterated isotopologues were synthesized using the deuterium substitution method described by Kydd and Mills[5]. The parent molecule was dissolved in D_2O and was allowed to stir for a few days. Then, liquid-liquid extraction was performed using chloroform as the organic solvent. After extracting the deuterated isotopologues into the chloroform solvent, excess solvent was evaporated from the molecules of interest using vacuum distillation. This process was repeated three times to ensure maximum deuteration of the molecule.

The experimental setup used to measure rotational transitions for these isotopologues is essentially identical to the setup used by our group to measure the parent molecule, 2-aminopyridine[6]. A sample containing the three isotopologues was loaded into a glass sample cell designed to fit the microwave spectrometer. This sample was heated to 85 ˚C to ensure sufficient vapor pressure to collect microwave measurements. The sample cell was connected to the microwave spectrometer on one end, and on the other end, it was connected to an argon carrier gas system. The backing pressure of argon gas was maintained near 0.7 atm during data collection. Inside the microwave spectrometer, a diffusion pump maintained the pressure of the chamber in the range of 10^{-6}-10^{-7} torr to allow the molecules entering the system to cool via supersonic expansion, inducing the population of the ground rotational and vibrational states of the isotopologues. Using these experimental conditions, an FID with a signal-to-noise ratio of 5:1 could be seen for the a-type 1_{01012}-0_{00123} transition (quantum numbers J, K_a, K_c, F_1, F_2, (F_3+F)) for the DH isotopologue in 75 pulsed-beam cycles. All of the isotopologues were present in the same sample cell since they could not be separated from one another. These molecules were pulsed into the chamber of the microwave spectrometer at a frequency of 2 Hz.

Calculations:

Structural parameters, rotational constants, and quadrupole coupling constants for the three deuterated isotopologues of 2-aminopyridine were calculated using Gaussian-16[7] on the University of Arizona HPC system[8], specifically, the Ocelote HPC which has 28 processors. The keyword "output=pickett" was used when submitting the calculations to receive microwave parameters upon completion, which includes the rotational constants (A, B, & C) as well as the quadrupole coupling constants for the ^{14}N and ^{2}H atoms within the isotopologues. The ab initio and DFT methods used for these calculations include B3LYP[9], MP2[10], and M11[11]. The basis sets that were used include def2-QZVPP[12], aug-cc-pVTZ[13], and aug-cc-pVDZ[13]. The results of the calculations of interest are shown in the following table (Table 1) in addition to the values of the rotational parameters obtained by Kydd and Mills[5]. One thing to note from these calculations is that the method and basis set that most closely produces experimental parameters for each isotopologue is MP2/aug-cc-pVTZ (method/basis set). This was expected because the Kydd and Mills values for the experimental parameters also most closely agreed with this calculation. The performed calculations were mainly of interest for their predicted values of the quadrupole coupling constants for ^{14}N and ^{2}H within the isotopologues. Knowing these parameters provided an estimate of the range of frequencies to scan due to quadrupole splitting which spanned roughly 2 MHz.

Rotational Parameter	**HD**				**DH**				**DD**			
	MP2/aug-cc-pVTZ	***B3LYP/aug-cc-pVTZ***	***M11/def2 qzvpp***	***Kydd and Mills***	***MP2/aug-cc-pVTZ***	***B3LYP/aug-cc-pVTZ***	***M11/def2 qzvpp***	***Kydd and Mills***	***MP2/aug-cc-pVTZ***	***B3LYP/aug-cc-pVTZ***	***M11/def2 qzvpp***	***Kydd and Mills***
A	5752.151	5779.433	5813.697	5730.930	5755.817	5782.013	5815.783	5734.440	5699.135	5726.116	5759.663	5678.500
B	2626.134	2631.606	2645.886	2624.650	2631.129	2636.317	2650.471	2628.800	2533.582	2537.488	2550.752	2531.000
C	1807.503	1811.143	1820.348	1802.840	1809.132	1813.008	1822.378	1804.630	1758.616	1761.388	1770.019	1753.800
(3 ^{14}N) $3/2*\chi_{aa}$	3.404	3.639	4.052	---	3.411	3.642	4.052	---	3.422	3.651	4.061	---
(3 ^{14}N) $1/4*(\chi_{bb}-\chi_{cc})$	1.408	1.599	1.800	---	1.400	1.595	1.797	---	1.407	1.599	1.800	---
(5 ^{2}H) $3/2*\chi_{aa}$	-0.047	-0.027	-0.017	---	---	---	---	---	-0.055	-0.036	-0.027	---
(5 ^{2}H) $1/4*(\chi_{bb}-\chi_{cc})$	0.054	0.063	0.066	---	---	---	---	---	0.055	0.065	0.068	---
(6 ^{2}H) $3/2*\chi_{aa}$	---	---	---	---	-0.068	-0.051	-0.040	---	-0.077	-0.060	-0.049	---
(6 ^{2}H) $1/4*(\chi_{bb}-\chi_{cc})$	---	---	---	---	0.076	0.076	0.073	---	0.077	0.078	0.075	---
(7 ^{14}N) $3/2*\chi_{aa}$	-0.198	0.038	-0.445	---	-0.556	-0.363	-0.445	---	-0.375	-0.160	-0.215	---
(7 ^{14}N) $1/4*(\chi_{bb}-\chi_{cc})$	-1.294	-1.278	-1.465	---	-1.234	-1.211	-1.390	---	-1.265	-1.245	-1.429	---

Table 1: Calculated and literature[5] values for the rotational constants and quadrupole coupling constants for the three isotopologues of deuterated 2-aminopyridine.

After calculating the molecular parameters and quadrupole coupling constants for each isotopologue, the SPCAT program in Pickett's program suite[14] was used to predict rotational transitions within the range of 4-15 GHz (within the range of the microwave spectrometer). The experimental rotational constants from Kydd and Mills and the quadrupole coupling constants from the predictions were input into SPCAT. One of the limitations of the SPCAT program is that it can use up to six quantum numbers at a time when labeling predicted rotational transitions. The presence of multiple atoms that exhibit quadrupole coupling (^{14}N and ^{2}H) introduced multiple F quantum numbers, which represented the total angular momentum of these atoms. Therefore, SPCAT combines the quantum numbers after the fifth one into the place of the sixth one. For example, the quantum numbers of J, K_a, K_c, F_1, F_2, F_3, F would become J, K_a, K_c, F_1, F_2, (F_3+F) in SPCAT. The work of resolving this issue and properly naming the transitions is incomplete at this point.

Results:

Finding the rotational transitions for each isotopologue was fairly straightforward due to the previously published values of the rotational constants (A, B, and C) for the isotopologues by Kydd and Mills. The most challenging part of finding these transitions was ensuring that all quadrupole components of each transition were measured. To ensure the successful identification of all signals, step sizes of 0.1 MHz were implemented when manually scanning for these transitions. Also, regions 0.5 MHz below the lowest frequency component of a transition and 0.5 MHz above the highest frequency component were scanned to ensure that the "wings" of each transition were correctly identified. Similar to the parent isotopologue of 2-aminopyridine[6], only the 0^+ vibrational state (the lower energy vibrational state) of each isotopologue was detected. As mentioned in that paper, the suspected reason for the inability to measure transitions for the 0^- is that the supersonic expansion of the molecules into the spectrometer substantially cooled the molecules so that there was insufficient population of the higher energy 0^- vibrational state. In total, 66 rotational transitions were measured for the deuterated isotopologues of 2-aminopyridine in the region of 4.4-10.9 GHz. These transitions primarily consisted of b-type transitions, but the 1_{01}-0_{00} a-type transition was measured for the DH and HD isotopologues. Multiple quadrupole components of these transitions were detected and measured. The measured transitions with assigned quantum numbers are provided in Tables 2-4 along with the results of the fit of these transitions to a rigid asymmetric rotor model.

DH				
J' K_a' K_c' F_1' F_2' (F_3'+F')	J" K_a" K_c" F_1" F_2" (F_3"+F")	ν_{obs} (MHz)	ν_{calc} (MHz)	Obs-Calc (kHz)
1 0 1 0 1 2	0 0 0 1 2 3	4426.288	4426.298	-10.18
1 0 1 2 3 3	0 0 0 1 2 2	4427.349	4427.383	-34.33
1 0 1 2 3 4	0 0 0 1 2 3	4427.388	4427.379	8.86
1 0 1 1 2 1	0 0 0 1 2 2	4428.052	4428.069	-17.47
1 0 1 1 2 3	0 0 0 1 2 3	4428.076	4428.068	7.87
1 0 1 1 2 2	0 0 0 1 2 3	4428.11	4428.067	43.87
2 0 2 3 3 4	1 1 1 2 2 3	5605.823	5605.834	-11.07
2 0 2 3 4 5	1 1 1 2 3 4	5605.884	5605.919	-35.03
2 0 2 3 4 3	1 1 1 2 3 2	5605.939	5605.985	-45.78
2 0 2 3 3 3	1 1 1 2 3 3	5606.271	5606.317	-46.34
2 0 2 2 3 4	1 1 1 1 2 3	5606.366	5606.372	-5.85
2 0 2 1 2 2	1 1 1 0 1 2	5606.485	5606.521	-36.13
2 0 2 1 1 2	1 1 1 0 1 1	5606.52	5606.447	72.99
2 0 2 1 2 3	1 1 1 0 1 2	5606.577	5606.547	29.97
2 0 2 2 3 2	1 1 1 1 2 1	5607.045	5607.053	-8.05
2 0 2 2 3 3	1 1 1 2 3 3	5607.404	5607.411	-7.07
1 1 1 0 1 2	0 0 0 1 2 3	7532.644	7532.591	53.13
1 1 1 2 3 3	0 0 0 1 2 2	7533.193	7533.174	19.73
1 1 1 1 2 1	0 0 0 1 2 2	7533.657	7533.667	-10.22
1 1 1 2 1 0	0 0 0 1 2 1	7533.758	7533.771	-13.11
1 1 1 2 3 2	0 0 0 1 2 1	7533.817	7533.782	34.58
1 1 1 2 1 2	0 0 0 1 0 1	7533.839	7533.803	36.13
1 1 1 2 3 4	0 0 0 1 2 3	7533.875	7533.805	69.44
1 1 1 1 2 3	0 0 0 1 2 2	7534.313	7534.3	12.26

1 1 1 1 2 2	0 0 0 1 2 3	7535.134	7535.114	19.98
9 5 4 10 11 12	9 4 5 10 11 12	29480.69	29480.88	-192.64
8 1 8 9 10 11	7 0 7 8 9 10	30745.93	30745.93	2.14
3 3 1 4 5 6	2 2 0 3 4 5	30808.35	30808.5	-146.13
7 5 2 8 9 10	7 4 3 8 9 10	30899.58	30899.89	-307.43
3 3 0 3 4 5	2 2 1 2 3 4	30966.75	30966.51	240.24
7 5 3 8 9 10	7 4 4 8 9 10	31114	31114.32	-323.46
9 0 9 10 11 12	8 1 8 9 10 11	34212.22	34212.28	-57.59
9 1 9 10 11 12	8 0 8 9 10 11	34297.87	34297.9	-32.18
4 3 2 5 6 7	3 2 1 4 5 6	34935.9	34936	-97.05

Table 2: Measured microwave transitions of the 0^+ state for the DH isotopologue along with deviations between the measured transitions and predicted transitions by the model. The RMS error of the fit is 4.25223 MHz. The transitions at 29GHz and greater frequencies come from the paper by Kydd and Mills[5]. The researchers in that paper were unable to detect quadrupolar splitting, so each frequency was assigned to the transition predicted to be most intense by SPCAT.

HD				
J' K_a' K_c' F_1' F_2' (F_3'+F')	J" K_a" K_c" F_1" F_2" (F_3"+F")	ν_{obs} (MHz)	ν_{calc} (MHz)	Obs-Calc (kHz)
1 0 1 0 1 2	0 0 0 1 2 3	4432.2	4432.199	1.19
1 0 1 2 3 3	0 0 0 1 2 2	4433.249	4433.231	18.43
1 0 1 2 3 4	0 0 0 1 2 3	4433.28	4433.318	-37.58
1 0 1 2 3 2	0 0 0 1 2 1	4433.322	4433.348	-25.73
1 0 1 1 2 1	0 0 0 1 2 2	4433.982	4433.924	58.37
1 0 1 1 2 3	0 0 0 1 2 3	4433.996	4434.005	-9.1
1 0 1 1 2 2	0 0 0 1 2 3	4434.021	4434.022	-1.09
2 0 2 3 3 2	1 1 1 1 1 1	5616.446	5616.425	21.53
2 0 2 1 2 2	1 1 1 1 2 3	5616.416	5616.403	12.41
2 0 2 1 1 2	1 1 1 1 1 2	5616.54	5616.525	14.73
2 0 2 1 1 1	1 1 1 2 2 1	5616.862	5616.936	-73.76
2 0 2 2 3 3	1 1 1 1 2 2	5617.265	5617.28	-14.41

2 0 2 3 4 4	1 1 1 2 3 4	5617.369	5617.371	-1.59
2 0 2 3 3 4	1 1 1 2 2 3	5617.587	5617.583	3.47
2 0 2 3 4 5	1 1 1 2 3 4	5617.664	5617.624	39.91
2 0 2 3 4 4	1 1 1 2 3 3	5617.956	5617.942	13.86
2 0 2 2 3 4	1 1 1 1 2 3	5618.079	5618.112	-33.49
2 0 2 2 3 3	1 1 1 2 3 2	5618.471	5618.472	-1.67
2 0 2 2 3 4	1 1 1 2 3 4	5618.605	5618.576	28.94
2 0 2 2 3 2	1 1 1 1 2 1	5618.764	5618.757	7.59
2 0 2 2 2 2	1 1 1 2 2 2	5619.017	5619.011	6.45
1 1 1 2 3 3	0 0 0 1 2 2	7538.523	7538.552	-29.76
1 1 1 0 1 0	0 0 0 1 2 1	7537.979	7537.972	6.7
1 1 1 2 1 0	0 0 0 1 2 1	7539.217	7539.184	33.44
1 1 1 1 2 3	0 0 0 1 2 2	7539.57	7539.588	-17.98
1 1 1 2 3 4	0 0 0 1 2 3	7539.151	7539.124	27.15
1 1 1 1 2 2	0 0 0 1 2 3	7540.302	7540.302	0.14
8 1 8 9 10 11	7 0 7 8 9 10	30776.84	30776.83	5.23
3 3 1 4 5 6	2 2 0 3 4 5	30828.51	30828.61	-104.85
3 3 0 3 4 5	2 2 1 2 3 4	30987.8	30987.53	270.97
7 5 3 8 9 10	7 4 4 8 9 10	31116.26	31116.2	57.16
6 5 2 7 8 9	6 4 3 7 8 9	31256.6	31256.68	-80.14
4 3 2 5 6 7	3 2 1 4 5 6	34960.31	34960.39	-76.49
4 3 1 5 6 7	3 2 2 4 5 6	35759.72	35759.72	-4.01

Table 3: Measured microwave transitions of the 0^+ state for the HD isotopologue along with deviations between the measured transitions and predicted transitions by the model. The RMS error of the fit is 1.08828 MHz. The transitions at 29GHz and greater frequencies come from the paper by Kydd and Mills[5]. The researchers in that paper were unable to detect quadrupolar splitting, so each frequency was assigned to the transition predicted to be most intense by SPCAT.

DD				
J' K_a' K_c' F_1' F_2' (F_3'+F_4'+F')	J" K_a" K_c" F_1" F_2" (F_3"+F_4"+F")	ν_{obs} (MHz)	ν_{calc} (MHz)	Obs-Calc (kHz)
2 0 2 1 1 2	1 1 1 1 2 3	5293.846	5293.82	26.26
2 0 2 3 3 4	1 1 1 2 2 3	5294.904	5295.021	-117.35
2 0 2 3 2 3	1 1 1 2 1 2	5295.35	5295.328	21.66
2 0 2 3 2 2	1 1 1 2 1 1	5295.455	5295.546	-91.31
2 0 2 2 3 2	1 1 1 2 1 1	5296.362	5296.368	-6.25
1 1 1 0 1 2	0 0 0 1 2 3	7431.161	7431.033	127.67
1 1 1 2 1 1	0 0 0 1 1 1	7431.721	7431.752	-31.16
1 1 1 2 1 2	0 0 0 1 2 1	7432.019	7431.991	27.53
1 1 1 2 3 3	0 0 0 1 2 2	7432.19	7432.313	-123.08
1 1 1 2 2 3	0 0 0 1 1 2	7432.337	7432.232	104.64
1 1 1 1 1 2	0 0 0 1 0 1	7432.794	7432.849	-54.81
1 1 1 1 0 1	0 0 0 1 1 2	7433.577	7433.199	377.56
2 1 2 3 2 2	1 0 1 2 2 2	10939.66	10939.71	-50.95
2 1 2 3 3 2	1 0 1 2 2 1	10939.84	10939.87	-35.44
3 3 0 3 4 5	2 2 1 2 3 4	30621.86	30621.69	170.13
4 3 2 5 6 7	3 2 1 4 5 6	34498.66	34498.69	-27.91
7 5 2 8 9 10	7 4 3 8 9 10	31164.66	31164.78	-120.11
7 5 3 8 9 10	7 4 4 8 9 10	31335.08	31335.31	-225.31
8 1 8 9 10 11	7 0 7 8 9 10	29931.34	29931.34	4.91
9 1 9 10 11 12	8 0 8 9 10 11	33376.05	33376.11	-59.22
9 5 4 10 11 12	9 4 5 10 11 12	29950.57	29950.48	86.83

Table 4: Measured microwave transitions for the 0^+ state of the DD isotopologue along with deviations between the measured transitions and predicted transitions by the model. The RMS error of the fit is 1.92242 MHz. The transitions at 29GHz and greater frequencies come from the paper by Kydd and Mills[5]. The researchers in that paper were unable to detect quadrupolar splitting, so each frequency was assigned to the transition predicted to be most intense by SPCAT.

Discussion:

After fitting the rotational transitions of the deuterated isotopologues in the 0^+ vibrational state using SPFIT[14], there is excellent agreement between the determined rotational constants (A, B, and C) and those obtained by Kydd and Mills[5] (Table 5). The somewhat large values of RMS error for the fits obtained for each isotopologue likely stem from the uncertainty introduced by the inclusion of the transitions measured by Kydd and Mills, which did not report a quadrupolar signature. Also, the resolution of our instrument was likely not high enough to measure all of the expected quadrupolar components of each transition. A more realistic picture of the resolution of our instrument compared to predicted transitions is shown in Figure 2.

Rotational Parameter	HD		DH		DD	
	Experimental	Kydd and Mills	Experimental	Kydd and Mills	Experimental	Kydd and Mills
A	5730.9474(57)	5730.93	5734.464325(236)	5734.44	5678.49911(126)	5678.5
B	2624.6544(52)	2624.65	2628.773291(124)	2628.8	2531.01769(116)	2531
C	1802.8382(36)	1802.84	1804.638166(129)	1804.63	1753.79856(83)	1753.8
(3 ^{14}N) 3/2*χ_{aa}	3.492(37)	---	3.61765(181)	---	2.7844(315)	---
(3 ^{14}N) 1/4*(χ_{bb}-χ_{cc})	1.5435(174)	---	1.52131(88)	---	1.5940(71)	---
(5 ^{2}H) 3/2*χ_{aa}	-0.450(116)	---	---	---	-0.4758(295)	---
(5 ^{2}H) 1/4*(χ_{bb}-χ_{cc})	-0.0671(297)	---	---	---	0.3797(78)	---
(6 ^{2}H) 3/2*χ_{aa}	---	---	-0.3376(40)	---	-0.5462(267)	---
(6 ^{2}H) 1/4*(χ_{bb}-χ_{cc})	---	---	-0.14021(108)	---	0.4565(77)	---
(7 ^{14}N) 3/2*χ_{aa}	-0.233(89)	---	-0.47161(271)	---	-0.21(100)	---
(7 ^{14}N) 1/4*(χ_{bb}-χ_{cc})	-1.2226(213)	---	-1.14771(69)	---	-1.43(100)	---

Table 5: Comparison of the experimental values of the rotational parameters and the Kydd and Mills[5] values of the rotational parameters.

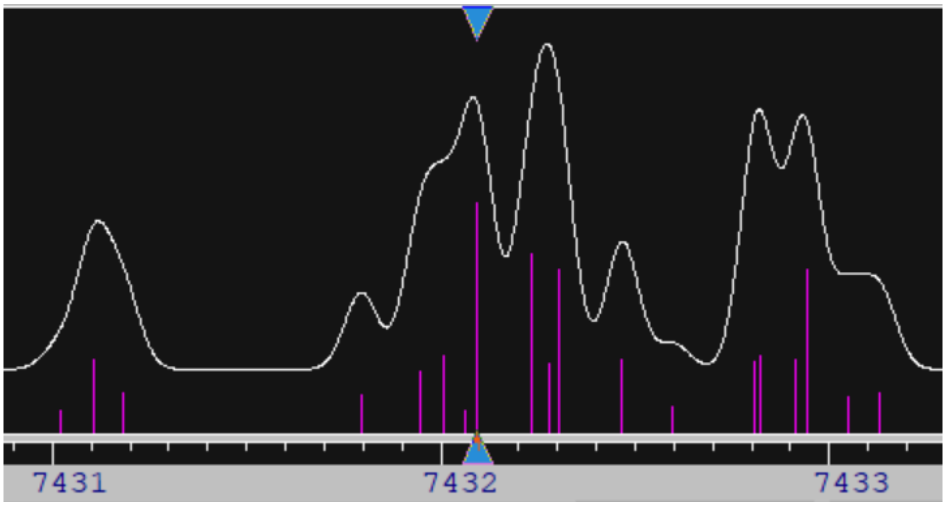

Figure 2: Image comparing the predicted structure of the quadrupole splitting (purple lines) to the likely structure detected by our instrument (white line). This figure shows the predicted signal structure of the 1_{11}-0_{00} b-type transition for the DH isotopologue. Figure obtained using the ASCP_L program[15].

Quadrupole coupling splitting within the three deuterated isotopologues of 2-aminopyridine was detected for each of the molecules. This allowed for the determination of the quadrupole coupling constants for the ^{14}N and ^{2}H atoms within two of the isotopologues (DH and DD) (Table 5). This was not the case for the DD isotopologue because the 1_{01}-0_{00} a-type transition was not measured. This specific transition is needed to reliably determine the values of the quadrupole coupling constants of the ^{14}N and ^{2}H atoms. For the DH and HD isotopologues, this transition was found, enabling the reliable determination of the quadrupole coupling constants. The calculation that most accurately predicted the values of the quadrupole coupling constants for the DH and HD isotopologues was the MP2 method with aug-cc-pVTZ as the basis set (Tables 1 and 5). The calculation that predicted the values of the quadrupole couplings constants the second best was B3LYP with aug-cc-pVTZ, and M11/def-QZVPP was the least accurate in predicting the quadrupole coupling constants for the molecules.

Future work of this project would involve the measurement of the 1_{01}-0_{00} transition for the DD isotopologue in order to reliably determine the quadrupole coupling constants of the ^{14}N and ^{2}H atoms within this molecule. The next step would then be to explore different hydrogen-bonded complexes that could be formed between 2-aminopyridine and other small organic molecules, such as formic acid. Eventually, deuterated isotopologues of 2-aminopyridine could be complexed with other small organic molecules, and the values of the quadrupole coupling constants of ^{14}N and ^{2}H atoms before and after complexation could be compared.

Conclusion:

Rotational transitions for three isotopologues of 2-aminopyridine with varying degrees of deuteration of the amino group were detected using a Fourier-transform microwave spectrometer in the frequency range of 4.4-10.9 GHz. Transitions were detected for only the 0^+ vibrational state of these isotopologues. The measured transitions were used to determine the quadrupole coupling constants of ^{14}N and ^{2}H within two of the isotopologues. These experimentally determined quadrupole coupling constants were compared to calculated values of these parameters, and the experimental values most closely agreed with the values predicted by the MP2/aug-cc-pVTZ calculation. Future work would involve the analysis of hydrogen-bonded complexes of 2-aminopyridine and its isotopologues with small organic molecules, like formic acid.

Description of Spectrometer 1 Program:

The program used to run Spectrometer 1 (Spec1), a Flygare-Balle type pulsed-beam Fourier transform microwave spectrometer, was built in LabVIEW 2019 SP1. The description of the instrument itself has been discussed in detail in previous papers by this group[4,16,17]. Therefore, a quick overview of the required tasks for the program is provided below in the following two figures.

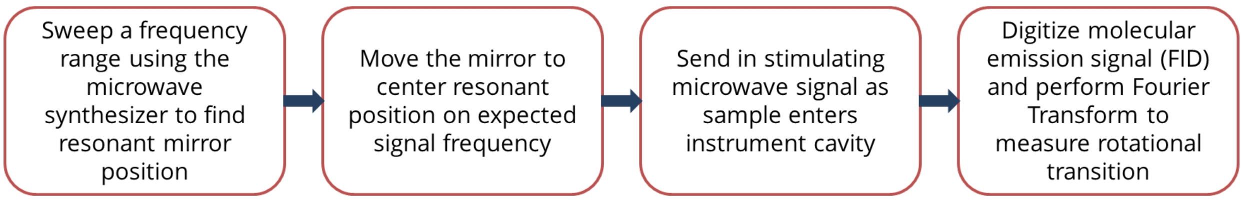

Figure 3: Flowchart describing the sequence of events completed by the program when determining a resonant mirror position (mode) followed by data collection and analysis.

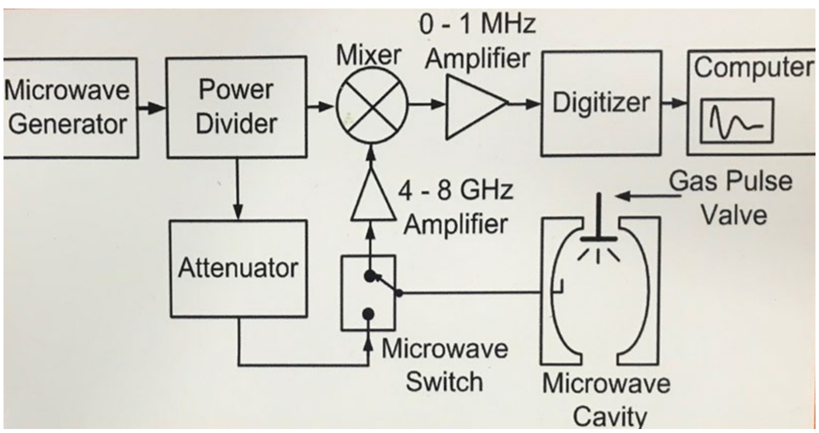

Figure 4: Block diagram showing the homodyne mixing circuit used in data collection.

The program begins by opening the Picoscope 2204A using a "subVI" (subroutine) created by Pico Technology specifically for LabVIEW called "PICO2K_Open.vi". Then, a while loop is encountered that surrounds the rest of the program and is accompanied by a stop button that will stop the program once clicked. After this, a case structure is encountered which is used to sweep the mode of the program. When the case is true, a flat sequence structure is reached which allows for sequential execution of desired tasks. First, the MCC DAQ device will stop collecting data, and it will clear the task that it was completing. In the following frame, a subVI called Sweep_better.vi is reached, which controls the sweeping of the cavity to look for a mode, and this subVI has a few controls that can be altered to change the sweeping of the mode. The “center frequency” control sets the frequency that the sweep is centered on. The “power level” control sets the power level used to sweep the cavity when looking for the mode, and this is often set to 13 dBm. The “sweep range” control sets the width of frequencies to be scanned for. If the “sweep range” is set to 200 MHz, for example, the program will scan 100 MHz below the center frequency and 100 MHz above the center frequency. When the case structure containing the sweep controls is set to false, an MCC DAQ subVI that sets the MCC DAQ to ready is enabled, allowing for data collection to take place only if this case structure is set to “false.”

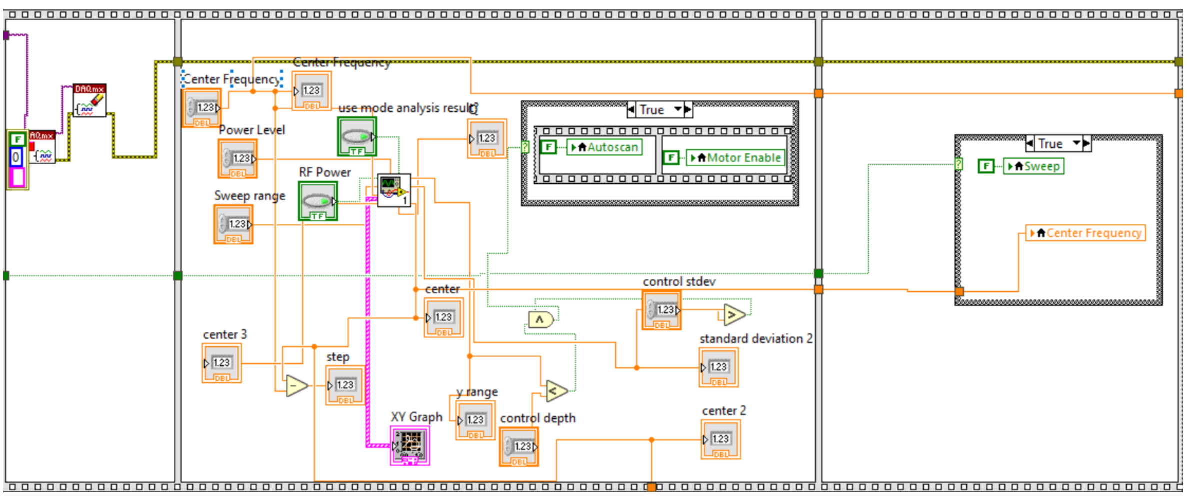

Figure 5: Block diagram illustrating the mode sweeping function of the program.

There is also a “use mode analysis result?” true/false statement which is used when employing Autoscan. When true, the program will track the mode as it moves along during an Autoscan, and it calculates the center of the mode “valley” using a Gaussian fitting function which is then reported by the “center” indicator. The “step size” of an Autoscan is determined by subtracting the previous center frequency from the current center frequency, and it is reported by the “step” indicator. There are also controls for setting the maximum standard deviation and the minimum depth of the Gaussian fitting function, which are used when enabling an Autoscan. If either of these conditions is not met, the program will stop running.

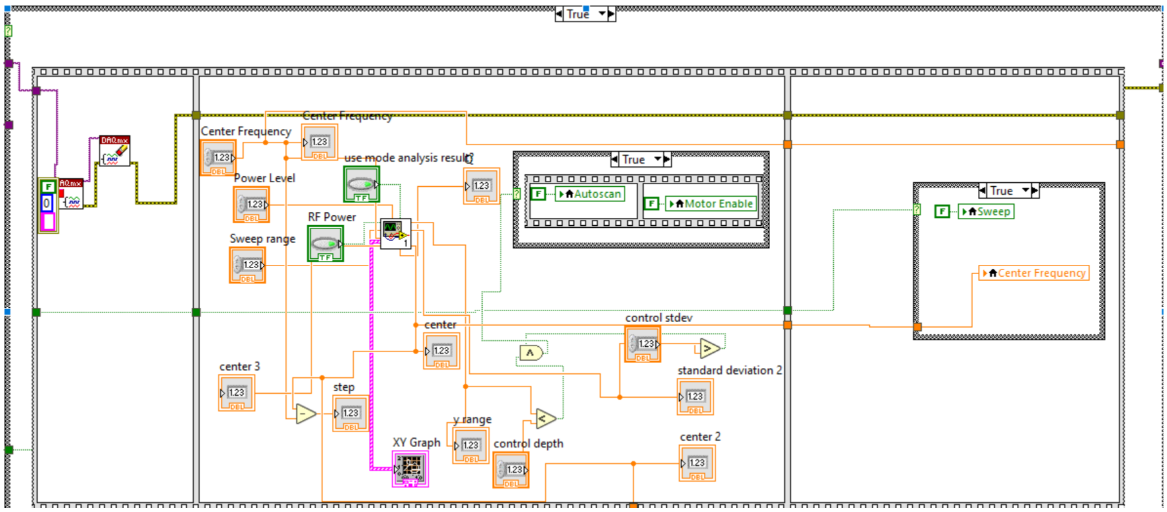

Figure 6: Image of a block diagram describing the part of the program used to sweep the mode.

Next, the “Take Data” component of the program is reached. This first involves a case structure, and when the structure is set to true, the program will collect data. When the structure is set to false, the ability to move the motor is enabled. This feature of the program uses a “knob” structure that controls the speed of the motor as it moves the mirror inside the instrument’s cavity. The direction of the motor can also be changed by inverting the polarity of the voltage applied to the motor using the MCC DAQ USB-1208LS.

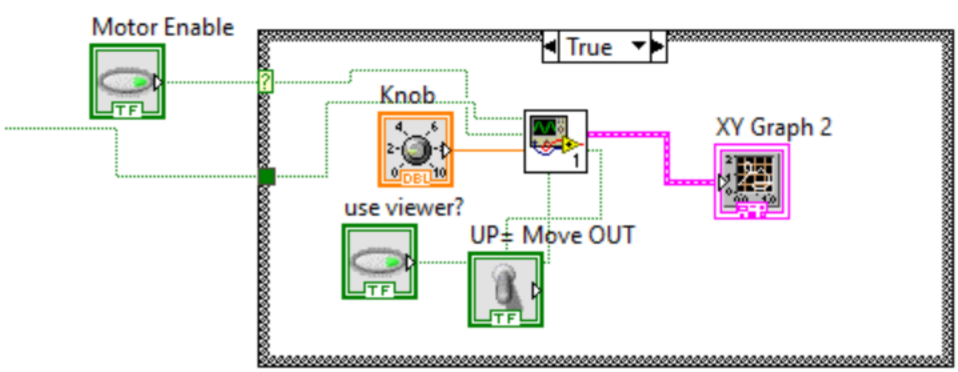

Figure 7: Block diagram from the program describing the motor moving functionality.

In the "true" case of this structure, many aspects of data collection can be altered. The power of the synthesizer in "data collection" mode can be changed by writing the desired power level to the synthesizer using string format and a "VISA write" function when the case of "RF power in Take Data" is set to true. Within the "Take_Data" subVI, there exist a few controls for data collection. The "valve to xmit delay" control sets a delay between the action of the valve and the transmission of data from the cavity. The "receive delay" control adds an extra delay to the beginning of data collection to allow the signal to leave the instrument. The number of cycles relates to the number of shots (or data values). The number of FIDs can be altered to allow for more data to be collected in the same amount of time, and the program sums these FIDs throughout the duration of data collection for a given frequency. Regarding the FIDs collected, the length of an FID is 512 points, so an array with values of 0 for each of its 512 indices is initialized, and the data collected by the instrument is added to this array. This data is then displayed as a waveform graph, producing a time domain function. A fast Fourier transform function is then used to transform the time domain into a frequency domain which records the response of the reflected microwave signal.

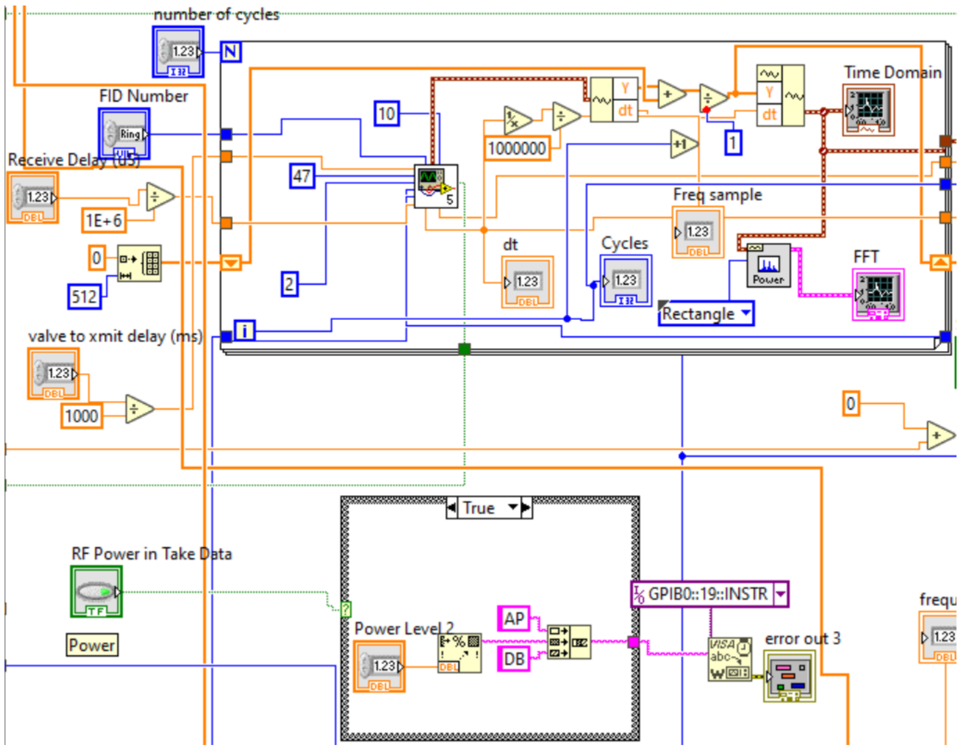

Figure 8: Block diagram describing the "take data" mode of the program.

Another case structure containing the function for saving measured data is reached, and the true/false button is called "Save File." When this is true, a string control is reached that is used to provide the prefix of the file name. When the program is not in Autoscan mode, a dialog box will open up and ask for a file name for the measured data. When the program is in Autoscan mode, the string control for the prefix of the file name will name a folder that will contain all of the data files collected during a scan. The data is written as a .plt file, and it contains voltage data, number of cycles, stimulated frequency, and sample frequency. When the program is terminated, the Picoscope is closed using a subVI, and the power level of -90 dBm is automatically written to the synthesizer.

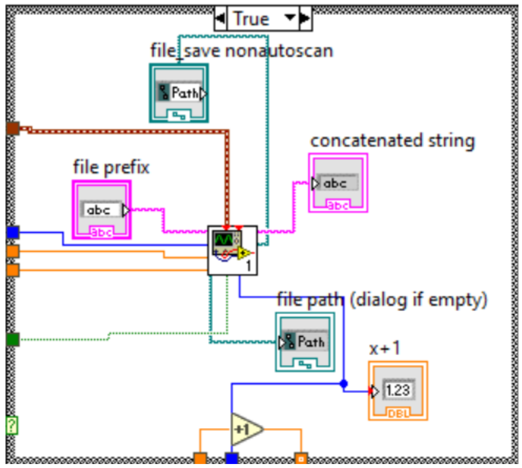

Figure 9: File saving function of the program.

As mentioned in the following section of this document, the Autoscan program enables the automation of the data collection process. This includes every aspect of data collection such as moving the mirror, sweeping the mode, taking data, and saving files. The way that this function works is by using local variables for each of these functions and sequentially carrying out these actions. The sequence that the program follows is: click Autoscan→sweep and track the mode→collect data→write the file and save the data into the prepared folder→move the motor→etc. One of the tools used to ensure that this sequence of events occurs consistently is by using a time delay between some of the events.

Microwave Spectrometer 1 Instructions

Measuring a Line:

First, the desired frequency must be set in the "center frequency" spot under the "Find the Mode" tab. Then, the "mode sweep" button must be double-clicked in order to set the center frequency in the synthesizer. Then, the motor must be moved to find a desirable mode. Under the "move motor" tab, first alter the "speed knob" to change the speed of the motor. The fastest speed is "10" on the knob, and the slowest speed is "0," which means that the motor is not moving. Setting the speed to 10 is used if the mode is known to be at a great distance away. Using a speed between 0 – 1 is helpful for finding modes that are a few MHz away. Before clicking the "move motor" button, one must first decide the direction that the motor will be moved. If the "motor direction" switch is moved to "up = move out," the motor will move in a direction that moves a mode to a lower frequency. If the "motor direction" switch is moved to "down = move in," the motor will move in which changes the mode to a higher frequency.

One method for finding a mode is to first set the desired frequency in the "Find the Mode" tab and put the "sweep range" to 200 MHz. After ensuring the "Rf power" button is clicked and set to 13 dBM, clicking the "mode sweep" button will cause the synthesizer to move through a range that is 100 MHz below the desired frequency and 100 MHz above the desired frequency. If you're lucky, a mode will be present in the sweep range, but if a mode is not seen, then the mode must be moved to a different location and the previous steps must be repeated. A mode is seen when there is a large "dip" in intensity in the intensity vs. frequency graph under the "Find the Mode" tab. The best modes are called "double modes," which means that there are two modes very close to each other (~2 to 4 MHz apart). Experimentally, the mode at a higher frequency (the "right" mode) has been found to always be a better mode than the left mode, so the “right” mode should be picked. Once a mode is seen in the intensity vs. frequency graph, move the motor until the mode is centered around a target frequency, and set the “sweep range” to 2 MHz. Once this happens, change the “center frequency” to be above or below the target frequency by about 100 KHz. For example, if the target frequency for the expected transition is 7564.400 MHz, the “center frequency” can be set to 7564.300 MHz or 7564.500 MHz. This is done because the Fourier Transform graph cannot detect a signal if the center frequency is the same as the frequency of the rotational transition.

Once the mode and center frequency are set, move to the “take data” tab. On this tab, one can set the number of cycles (or shots), number of FIDs, receive delay, valve to xmit (transmit) delay, and synthesizer power level. The receive and valve to xmit delay and power level are empirically found for a molecule and usually are optimized to yield the best signal strength. The number of cycles is also optimized for each molecular system, but ~100 shots are usually sufficient for seeing weaker signals. The number of FIDs is usually set to 4. Once all the parameters on the “take data” tab are set, the “RF power in Take Data” button should be clicked to ensure that the set power value is sent to the synthesizer. Then, the “Take Data” button is clicked, upon which the instrument will begin taking data for the allotted number of cycles. If the “Take Data” button is not clicked again, the instrument will continue to take data. Once the “Take Data” button is clicked again, the instrument will continue to take data until the last cycle number is reached.

If the user wishes to save the measured line, one must click the “save file” button on the “Take Data” tab while the “take data” button is clicked. After the last cycle is reached, the program will open up a box that asks for the name and location of the file to be saved. Any name can be given for the file, but it is important that the extension ".plt" is added to the end of the file name. This allows the data file to be analyzed using the lab's data analysis programs.

Using Autoscan:

The purpose of the Autoscan feature of the program is to automate the data collection process so that data can be collected overnight, over a weekend, or even just for a few hours without manual input. To first set up a scan, a mode for the starting frequency must be found using the steps mentioned in the previous section. Once the mode is found, set the number of cycles to something small like 10 and click the "Take Data" button. Then, be sure to click the "use mode analysis result?" button under the "Find the Mode" tab. Doing this allows the mode to "track" with the autoscan as it moves along. Then, set the motor to move in the desired direction of the scan ("move out" to decrease in frequency or "move in" to increase in frequency). Set the knob that dictates motor speed to something in the range of 0-2. This will likely need to be tinkered with, but this is a good starting point. Then, go to the "Autoscan" tab and name the file for the data to be collected in the "file prefix" text field. It is suggested that you include the starting frequency and which direction the scan is going to move (up or down in frequency). The program automatically adds the date to the end of the file. The "Autoscan" button should then be clicked on.

At this point, the "motor enable," "take data," and "save file" buttons should all be clicked on automatically by the Autoscan program. However, if one of them is not on, be sure to turn it on. The program should then start taking data for the number of cycles specified, and after the number of cycles is reached, the program will move the motor once and then sweep for the mode. Under the "Autoscan" tab, the difference between the last mode frequency and the current mode frequency is shown as the "step", and ideally, this should be in the range of 160-220 kHz

(.16-.22 MHz) to ensure that no rotational transitions are missed. If the step size is too large, decrease the motor knob to a slower speed, and if it is too small, increase the motor knob to a faster speed. If changing the motor knob doesn't change the step size much, the voltage on the motor can be manually adjusted on the motor power supply, but this should be done as a last resort. Once a satisfactory step size is reached and is somewhat consistent, the number of cycles should then be increased to the desired amount. The program can then be left alone to take data.

Another feature of the program that is particularly useful for Autoscan is found under the "Find the Mode" tab. The standard deviation and mode depth indicators are two measures of the quality of the mode. In general, a small standard deviation and large mode depth are best for collecting data. A maximum value for standard deviation and a minimum value for mode depth can be set for a scan to ensure that a good mode is being used. If the mode exceeds the maximum standard deviation or falls below the minimum mode depth, the Autoscan feature will stop, and the instrument will stop collecting data. This feature is extremely helpful because it minimizes sample waste and ensures that collected data is not meaningless.

To stop an Autoscan, one should first unclick the Autoscan button under the Autoscan tab. The program should finish taking data for the current cycle and then stop once the cycle is complete. However, it is important that the user ensures that the "Motor Enable," "Take Data," and "use mode analysis?" buttons are all unclicked after the Autoscan is done. Once this is done, the data can be removed from the computer and subsequently analyzed using the ScanViewer program created in MATLAB by Kristen Roehling.

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