Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplemental Information for:
High Throughput Chirped Pulse Fourier-Transform Microwave Spectroscopy of Ethanol and Water Clusters
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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			
10: 12 2 10 11 2 9	13336.93000	13336.91241	0.01759	0.10000	0.00000	13336.91612	0.01388	0.5000
11: 12 3 10 11 2 9	13336.93000	13336.91983	0.01017	0.10000	0.00000	13336.91612	0.01388	0.5000
12: 13 0 13 12 0 12	12589.25000	12589.21074	0.03926	0.10000	0.00000			

ORMALIZED 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	
1	10000	A	996.292(39) -0.000
2	20000	B	802.643(103) 0.000
3	30000	C	469.3070(208) -0.0000
4	200	-DeltaJ	-0.01512(92) -0.00000
5	2000	-DeltaK	-0.03642(235) -0.00000
6	1100	-DeltaJK	0.0476(33) 0.0000
7	40100	-deltaJ	-4.54(41)E-03 -0.00E-03
8	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

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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
)RMALIZED 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
1       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

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: 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
)RMALIZED 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
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1       10000         A        2709.384( 71)          0.000
2       20000         B        923.4670(172)         -0.0000
3       30000         C        724.8563(133)         -0.0000
4         200    -DeltaJ         0.02092( 87)        -0.00000
5        2000    -DeltaK         0.03112(171)        -0.00000
6        1100    -DeltaJK        -0.05419(262)         0.00000
7       40100    -deltaJ         -0.01409( 54)         0.00000
8       41000    -deltaK          0.02243(117)         0.00000
MICROWAVE AVG =      -0.000221 MHz, IR AVG =        0.00000
MICROWAVE RMS =       0.117729 MHz, IR RMS =        0.00000
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: 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
NORMALIZED 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
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                        NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
1       10000         A         2406.62( 32)          0.00
2       20000         B        1068.142( 73)          0.000
3       30000         C        810.0104(162)         -0.0000
4         200    -DeltaJ          0.1517( 64)        -0.0000
5        2000    -DeltaK          0.1359( 65)        -0.0000
6        1100    -DeltaJK        -0.2891(129)         0.0000
7       40100    -deltaJ         -0.05870(255)         0.00000
8       41000    -deltaK          0.02981(211)        -0.00000
MICROWAVE AVG =      -0.001192 MHz, IR AVG =        0.00000
MICROWAVE RMS =       0.082029 MHz, IR RMS =        0.00000
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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.

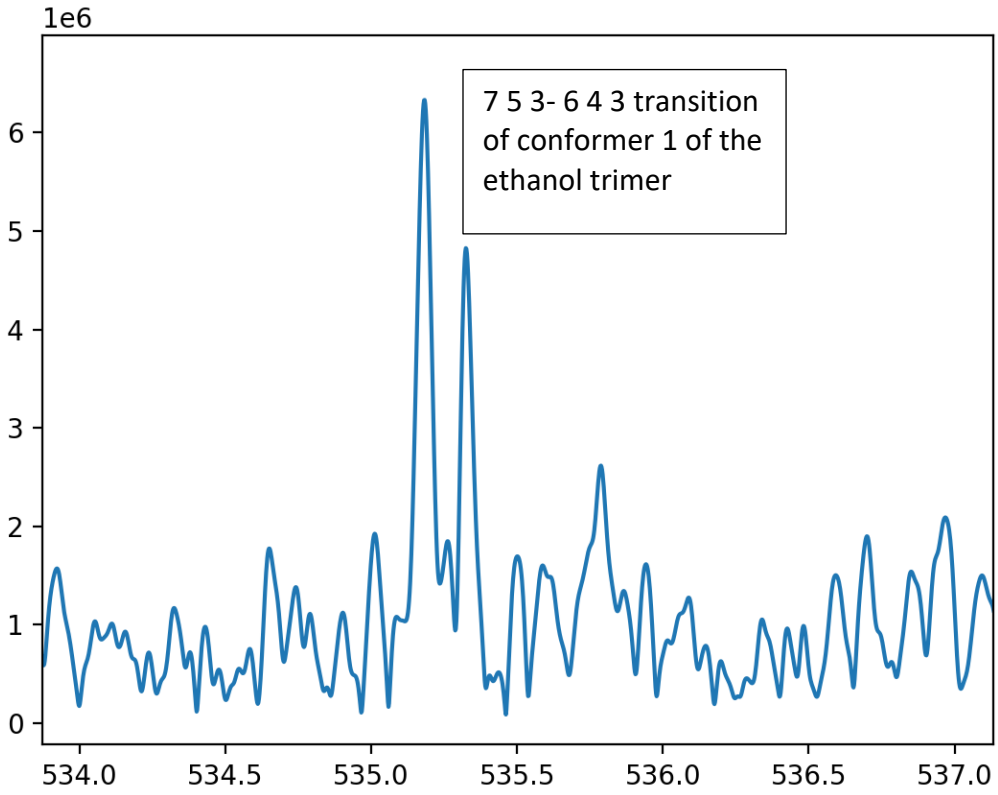
```
13  0 13  12  0 12   S 1  V 1   12.827487   6.5071   .0000  25.0000   .0000   .0597  B 1  K  0  0  t  1  1
13  1 13  12  0 12   S 1  V 1   12.827487  10.9999   .0000  25.0000   .0000   .0597  B 1  K -1  0  t  2  1

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

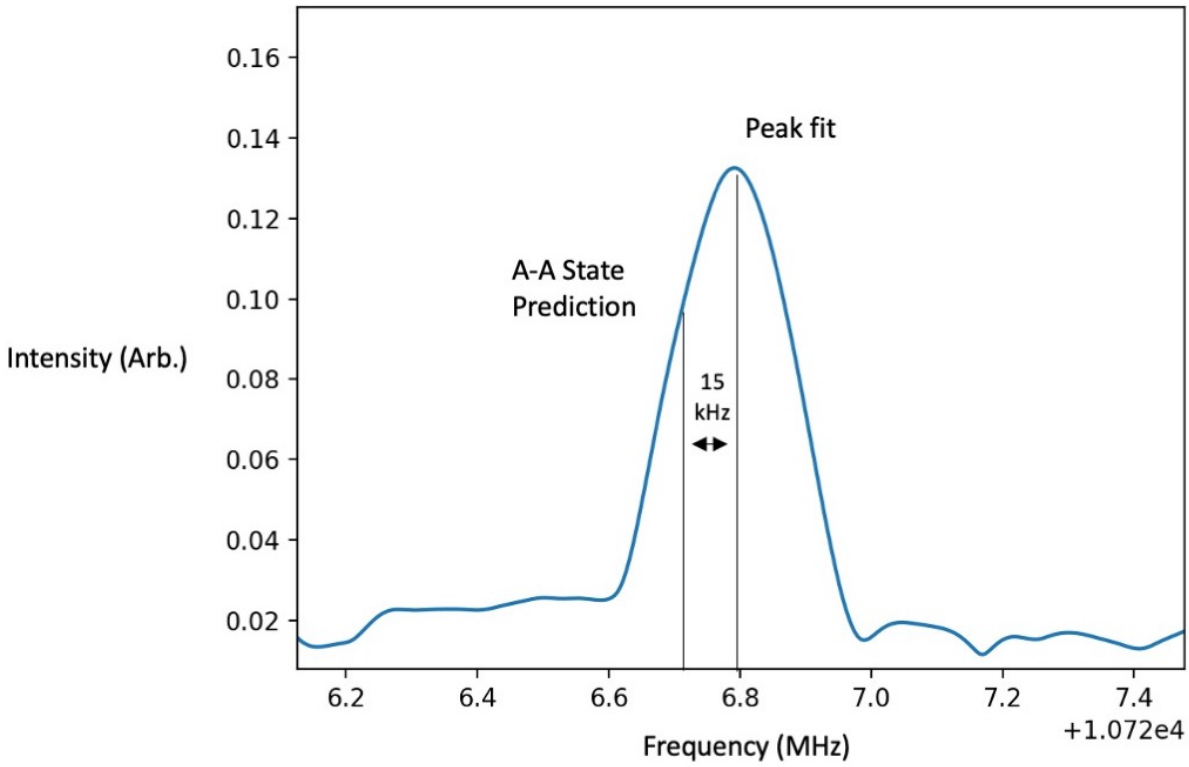
12 0 12 11 0 11 S 1 V 1 11.842965 1.0817 .0000 23.0000 .0000 .0553 B 1 K 0 0 t 1 1
12 0 12 11 0 11 S 2 V 1 11.842959 16.0887 .0000 23.0000 .0000 .0553 B 1 K 0 0 t 1 1
12 0 12 11 0 11 S 3 V 1 11.842959 16.0887 .0000 23.0000 .0000 .0553 B 1 K 0 0 t 1 1
12 0 12 11 0 11 S 4 V 1 11.842953 16.0887 .0000 23.0000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

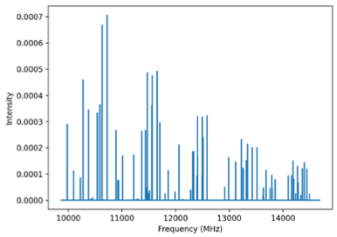
Asymmetry of line at 12536 MHz:



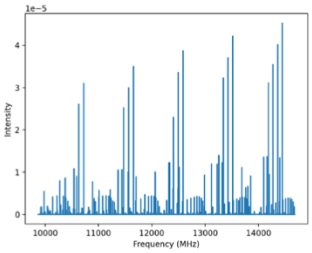
In addition, XIAM predictions of error were compared to peaks fit, to show that with increased sensitivity to fit only the AA states, error in spfit would follow expected experimental error on the order of ~10s of kHz. For example, this peak at 10726 MHZ for conformer 2 of the ethanol trimer has a predicted 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.



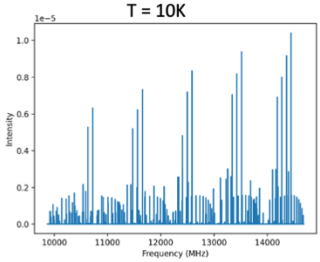
Finally, rotational temperature of the experimental expansion was approximated by comparison to spectra simulated with the program PGOPHER. Here is a comparison of simulated spectra at different temperatures with real data, used to assign the approximate rotational temperature of the supersonic expansion. 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.



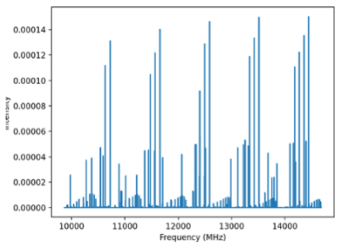
T = 1K



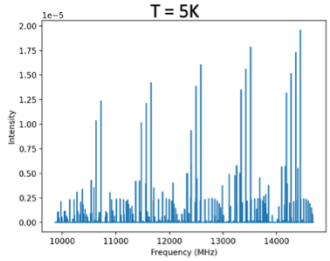
T = 10K



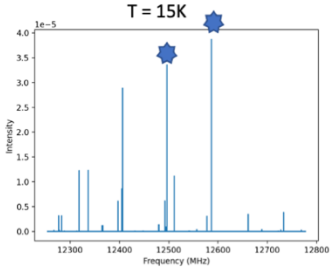
T = 20K



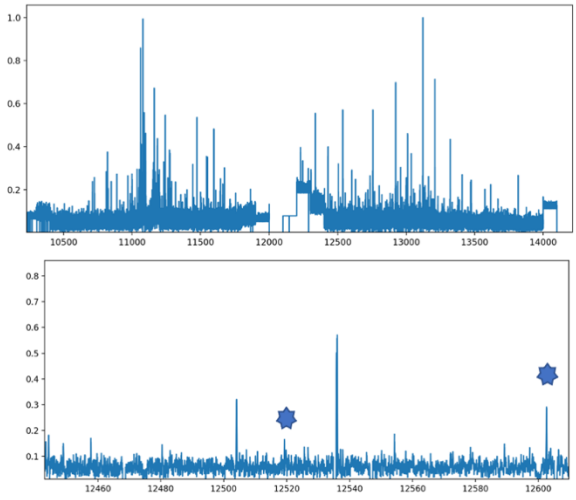
T = 5K



T = 15K



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.