Combined Microwave and Millimeter Wave Studies of the Molecules Hydroxyacetone and Lactonitrile

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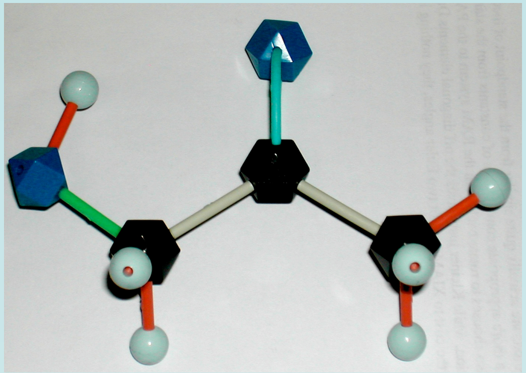
Why these two molecules?

- Test out the newly built FTM Spectrometer
  - Hydroxyacetone started in March 2005
    - Astrophysical implications
      - Exhibits the next level of complexity for “sugar” type molecules
      - Difficult methyl top problem—could account for U-lines
      - Similar to the recently discovered acetamide
    - We supposedly knew the frequencies
    - High vapor pressure liquid easy to get in the gas
    - First of two papers just submitted (or just about to be)
  - Lactonitrile started a few days before the deadline
    - Another methyl top, but this one has no resolved E-species
    - Hyperfine practically gives away the microwave lines
    - High vapor pressure liquid easy to get in the gas phase
    - Two stable conformers (dynamical spectroscopy)
    - Astrophysically relevant acetaldehyde cyanohydrin

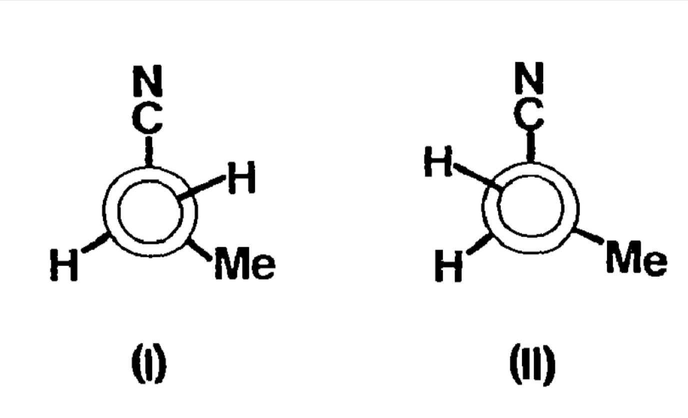
Previous Studies

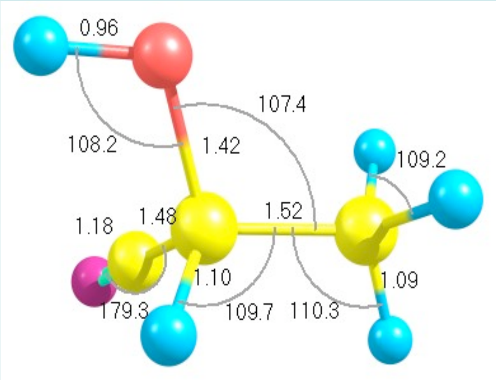


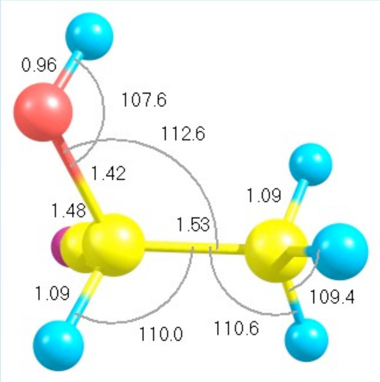
- Hydroxyacetone
  - Kattija-Ari and Harmony 1980 (Inter. J. Quan. Chem.:Quant. Chem. Sym., 14, 443)
    - A-state 26 to 40 GHz (43 lines)
    - E-state (10 lines; several misassigned)
    - Dipole moments (μ_a = 2.22 D; μ_b = 2.17 D)
    - Low Barrier internal methyl rotor
  - Braakman, Drouin, Widicus and Blake 2005 (60th Inter. Sym. on Mol. Spec.)
    - A-state 85 to 115 and 220 to 376 (578 lines)
    - E-state (288 lines)
    - Astronomical search 1 mm ($N_{tot} < 8 \times 10^{14}$ cm^{-2})

Previous Studies: Lactonitrile

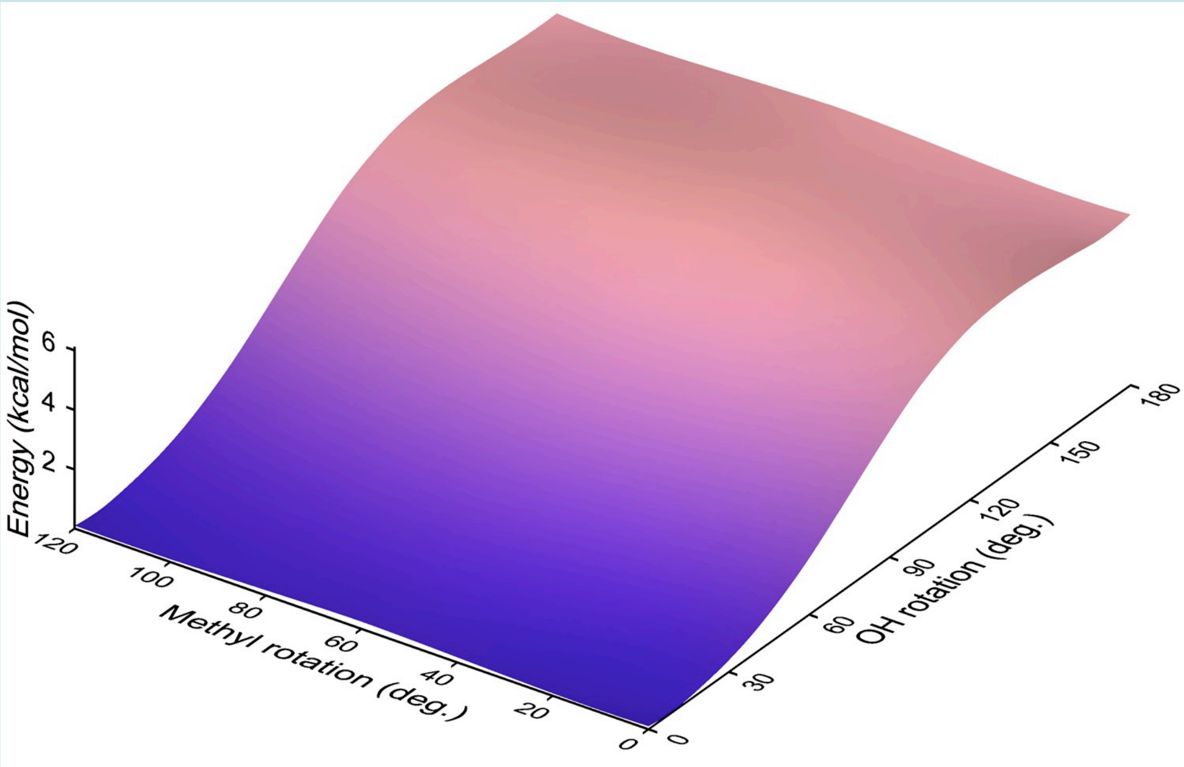
- Acetaldehyde cyanohydrin
- Corbelli and Lister 1981 J. Mol. Struct., 74, 39
  - Two stable gauche rotamers
  - Measured a few a-type transition in each between 13 and 37 GHz
  - Course rotational constants
  - Not much structural information
- Their gauche rotamers were approximately correct

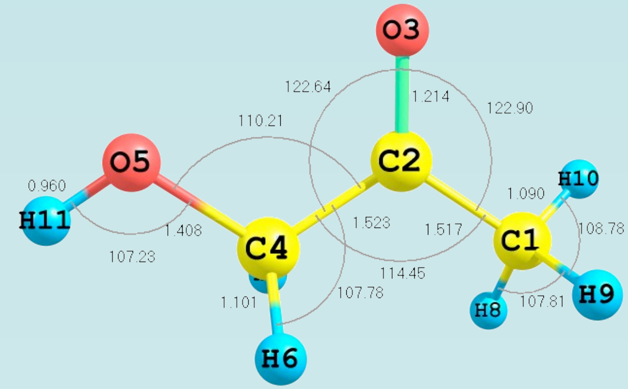


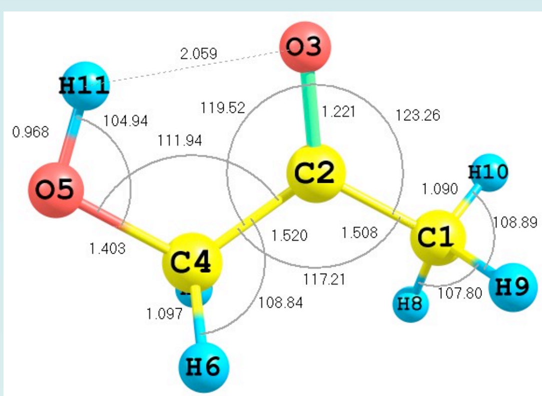




Ab Initio Calculations: Hydroxyacetone

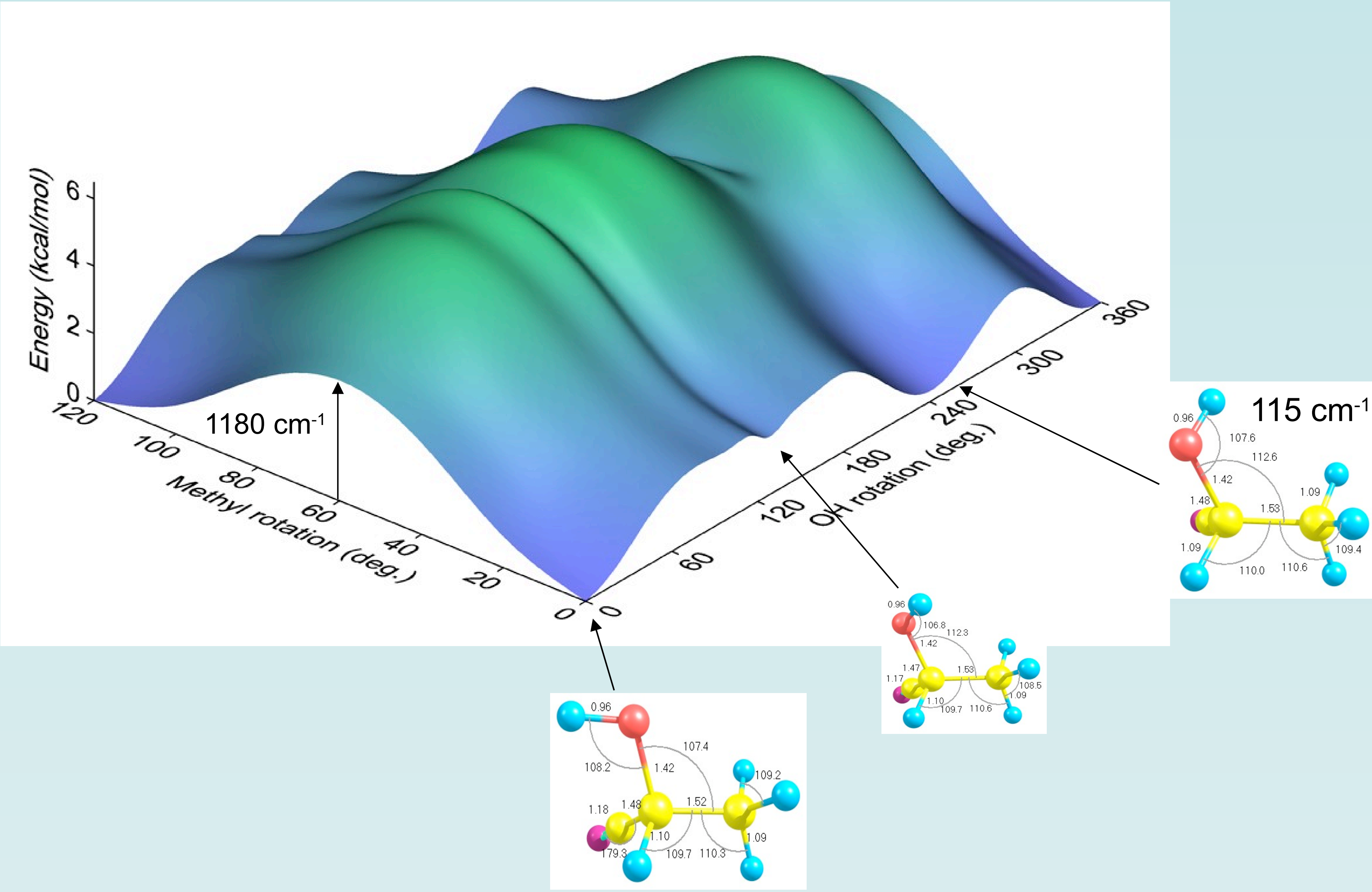




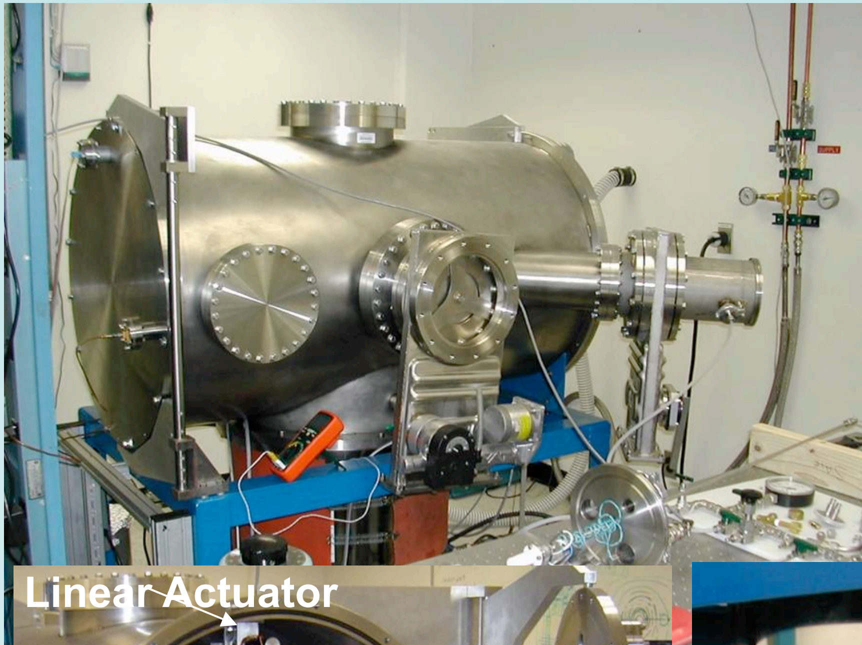


MP2/6-311+G** Geometry Optimization
CCSD (T)/6-311+G** Single Point Calcs.
Conformer II not stable
Methyl rotation barrier ~57 cm^{-1}

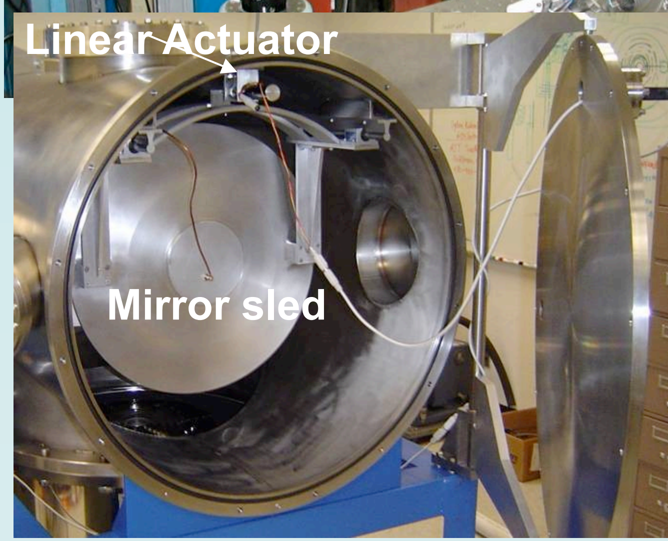
Ab Initio Calculations: Lactonitrile

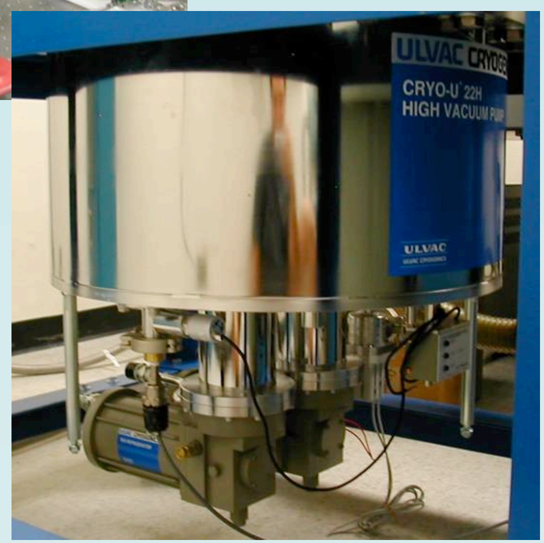


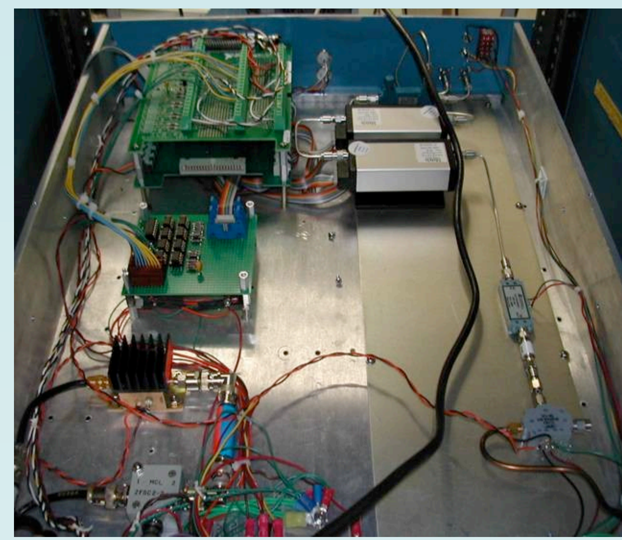
FTM Spectrometer



- 20” mirrors (4 to 20 GHz operation)
- Upgrade to 40 GHz by August
- Complete computer control and tuning
- NI timing electronics and DAQ
- Modified FTMW++ (Jens Grabow)
- Two 8” gate valves for nozzle
- Radiation/magnetic shield planned
- 22” cryopump (14000 liters/sec Ar)

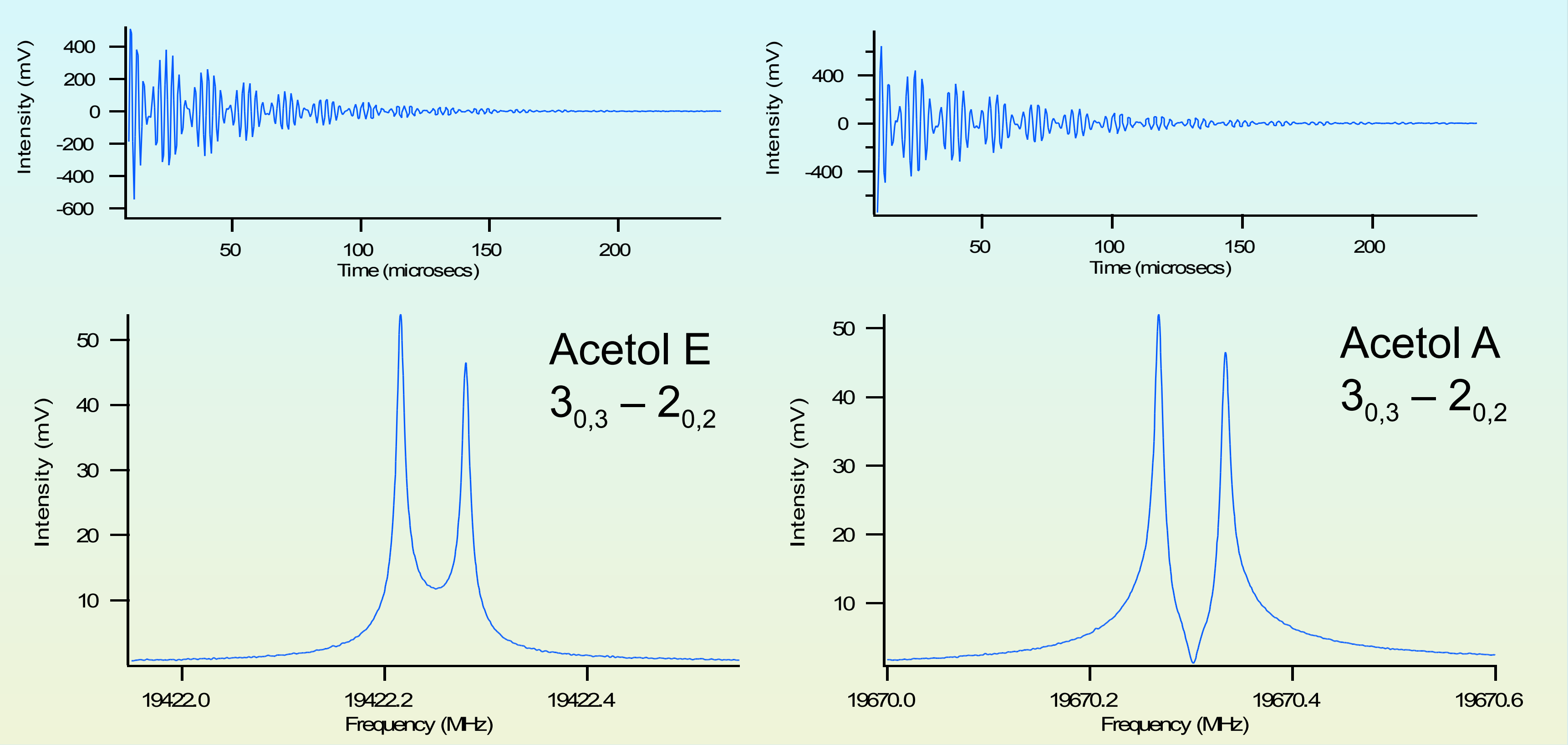






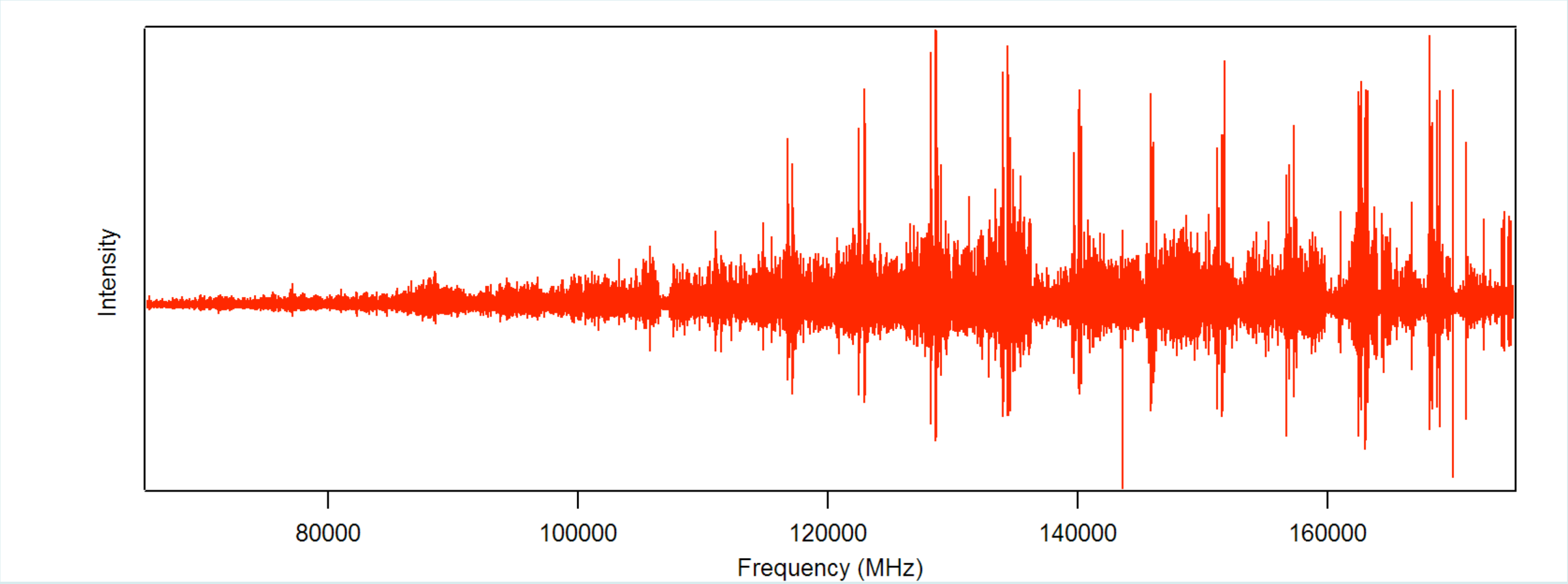
Microwave Data: Hydroxyacetone

46 microwave lines were measured to an accuracy of about 2 kHz
S/N > 100 on most of the lines
Microwave lines were necessary for assigning the millimeter wave data and to "lock-in" the E-state parameters

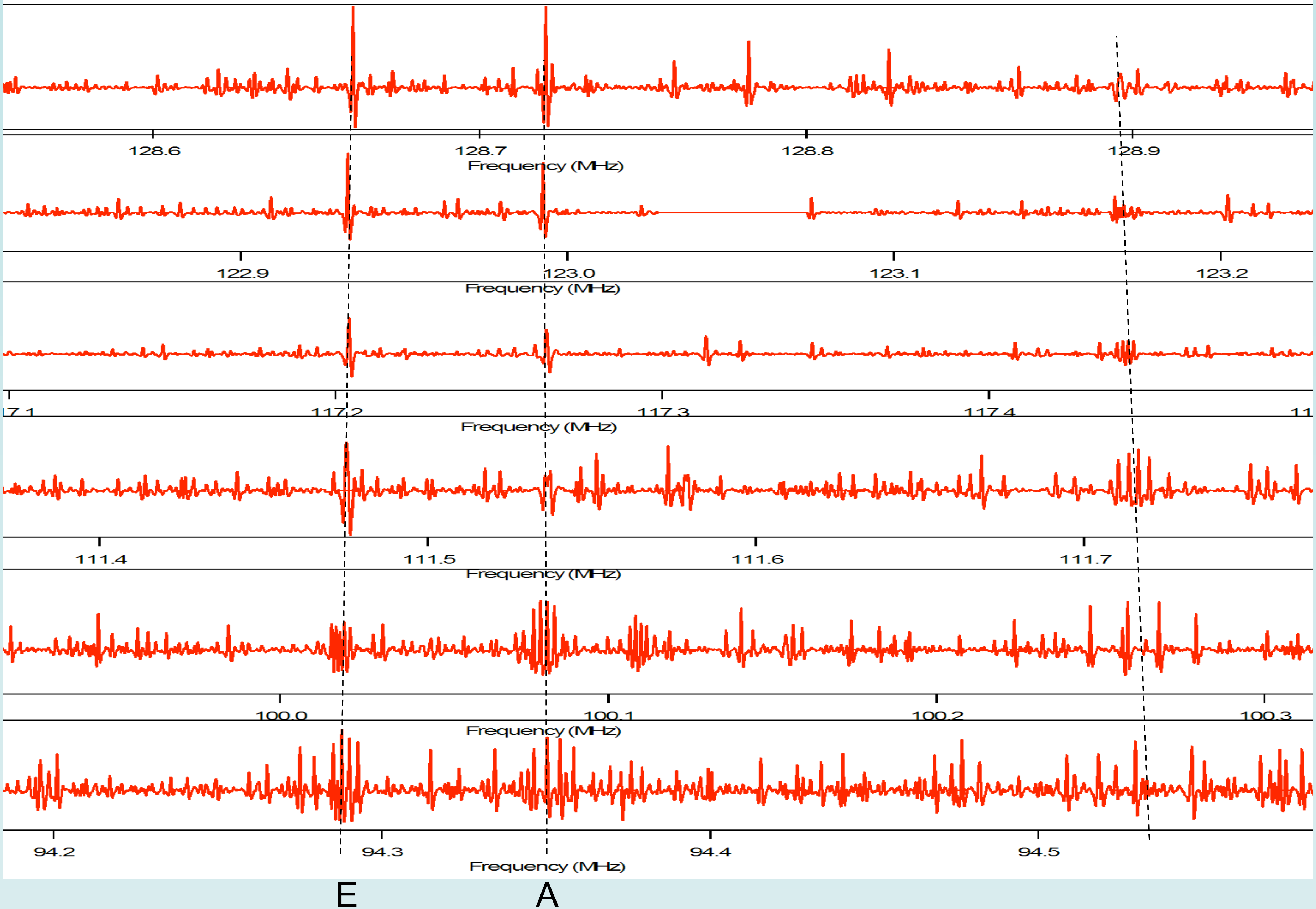


Millimeter Wave Data

Covered 65 to 175 GHz contiguously
Stitched together ~1800 spectra with a total of 1,150,000 data points
Each scan took about 5 minutes to acquire
Room temperature spectrum strong above 120 GHz owing to the collapsed asymmetry splittings
Strongest lines separated by about (B+C) or 4 GHz



Hydroxyacetone J = 16 to 21



Rho-axis method Hamiltonian

Rotation-Torsion Hamiltonian
ρ -Axis Method (RAM)

$$\hat{H} = \hat{H}_{rot} + \hat{H}_{tors} + \hat{H}_{dist}$$

$$\hat{H}_{rot} = \tfrac{1}{2}(B+C)(\hat{P}_b^2 + \hat{P}_c^2) + A\hat{P}_a^2 + \tfrac{1}{2}(B-C)(\hat{P}_b^2 - \hat{P}_c^2) + D_{ab}(\hat{P}_a\hat{P}_b + \hat{P}_b\hat{P}_a)$$

$$\hat{H}tors = F(\hat{P}_\gamma - \rho\hat{P}_a)^2 + \tfrac{1}{2}V_3(1 - \cos 3\gamma)$$

RAM code provided by Isabella Kleiner
History of the code:

C I.KLEINER AND M.GODEFROID (FREE UNIVERSITY OF BRUSSELS,
C 50, AV. F-D. ROOSEVELT, 1050 BRUSSELS, BELGIUM, 1987-91)

C jth added two cards here

C 30 sep MAB Today is the end of the common block.
C 4 oct 05 MAB - Implement torsional basis sorting of M.A. Mekhtiev and J.T. Hougen,
C J. Mol. Spec., 187, 49-60, (1998), Ilyushin (2004), J. Mol. Spec., 227, 140

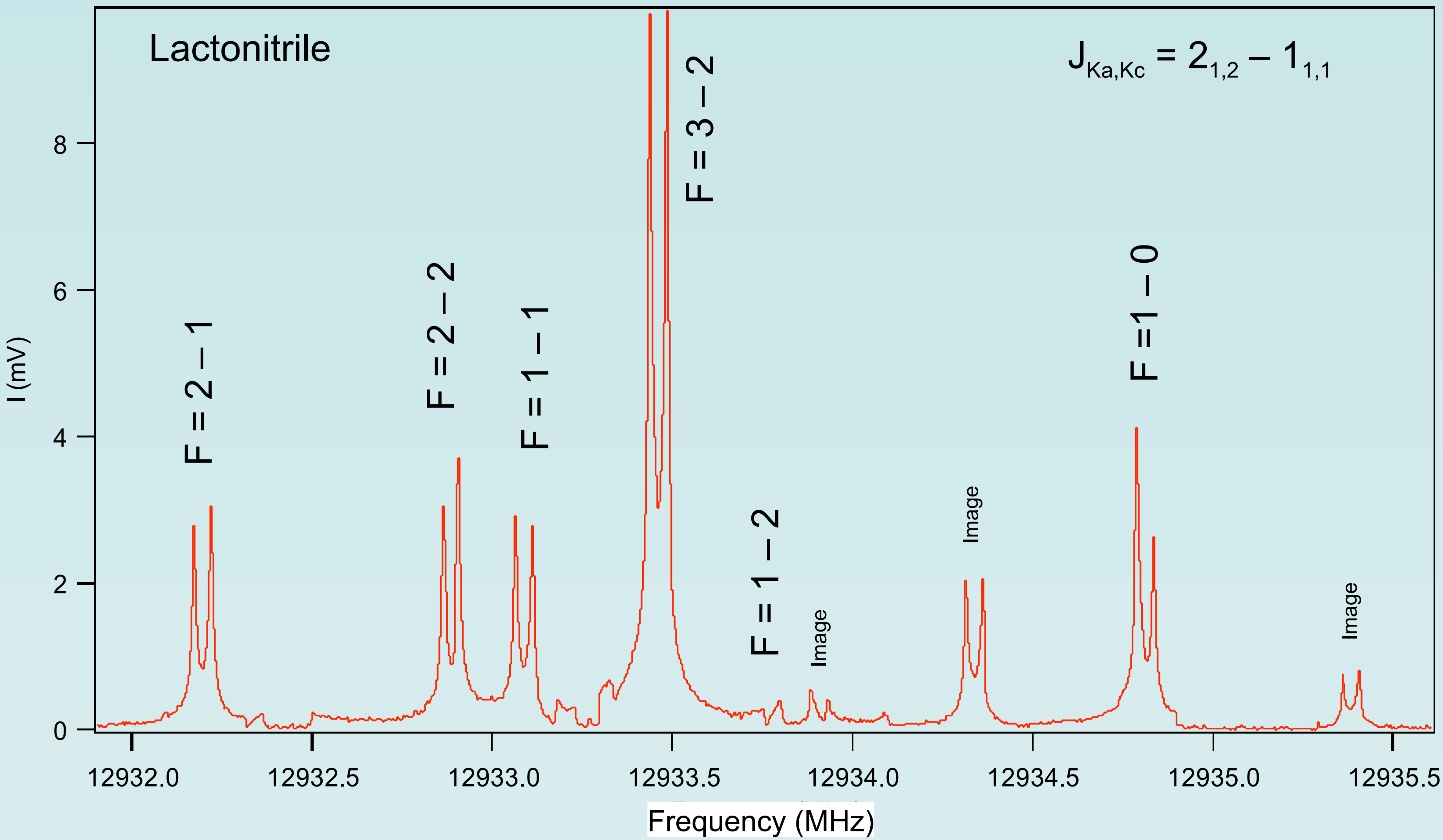
Eigenvector Labeling Problem

- "Old School" energy ordering doesn't work for energies above the barrier
- Since the levels are *K*-dependent, a given torsional basis cannot be associated with a single eigenvector
- Ask Jon Hougan at the Picnic

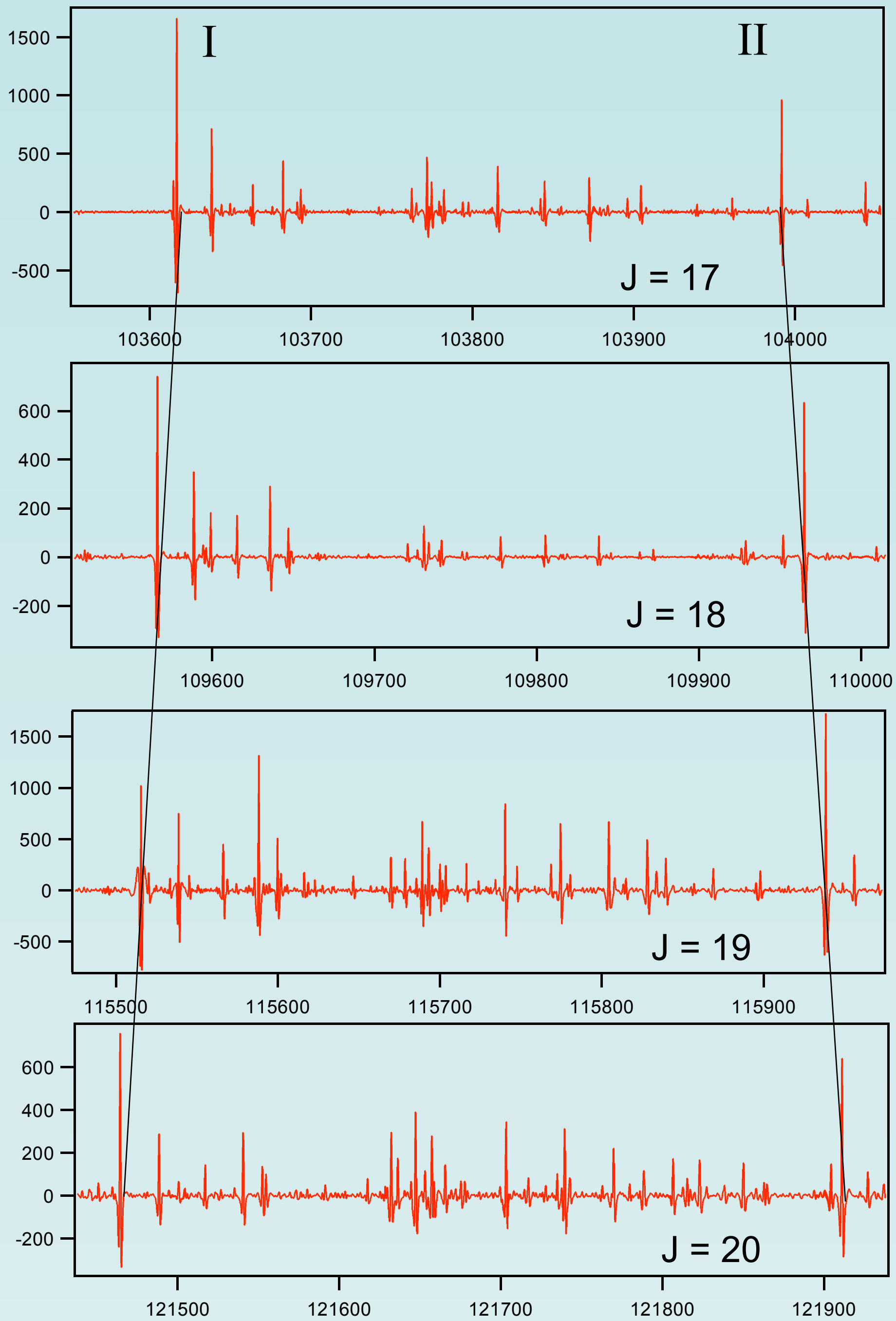
Fitted Rotational Constants for Hydroxyacetone

Leading order parameters (21 total parameters)			
Parameter	Operator	This Work	Kattija-Ari et al.
V_3	$(1/2)(1-\cos 3\gamma)$	65.3560(22) cm^{-1}	68(4) cm-1
F	P_γ^2	159.1189(40) GHz	157.931 fixed
ρ	$P_\gamma P_a$	0.0587793(26) unitless	nd
A (diagonalized)	P_a^2	10074.875(51)	10069.410(57)
B (diagonalized)	P_b^2	3817.2550(90)	3810.412(8)
C (diagonalized)	P_c^2	2866.6157(100)	2864.883(4)
D_{ab}	$\{P_a,P_b\}$	1089.287(44)	nd
$\Delta I=I_c-I_a-I_b$		6.5 amu $Å^2$	6.4 amu $Å^2$
Total number of lines		1145 (740 A; 405 E)	53
Microwave RMS		4 kHz	A-state 20 kHz
Millimeter wave RMS		90 kHz	E-state 9 MHz

Microwave Data: Lactonitrile



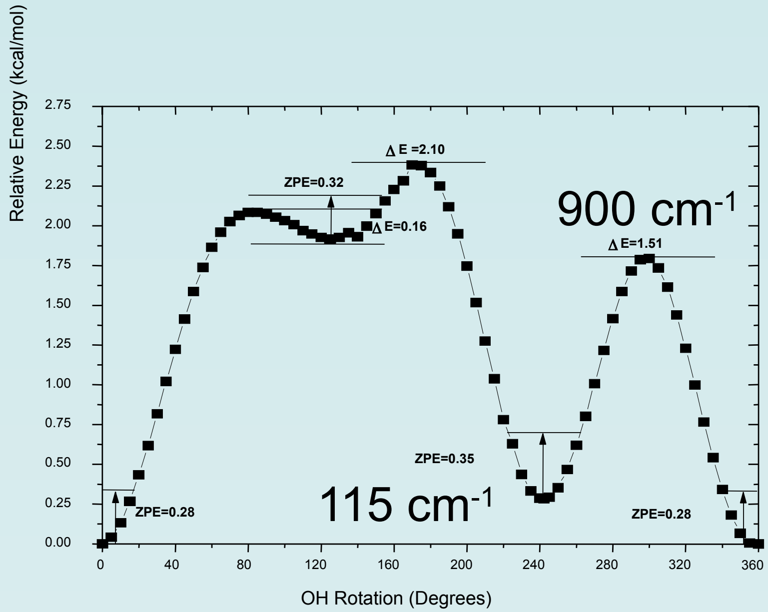
Millimeter Wave Data



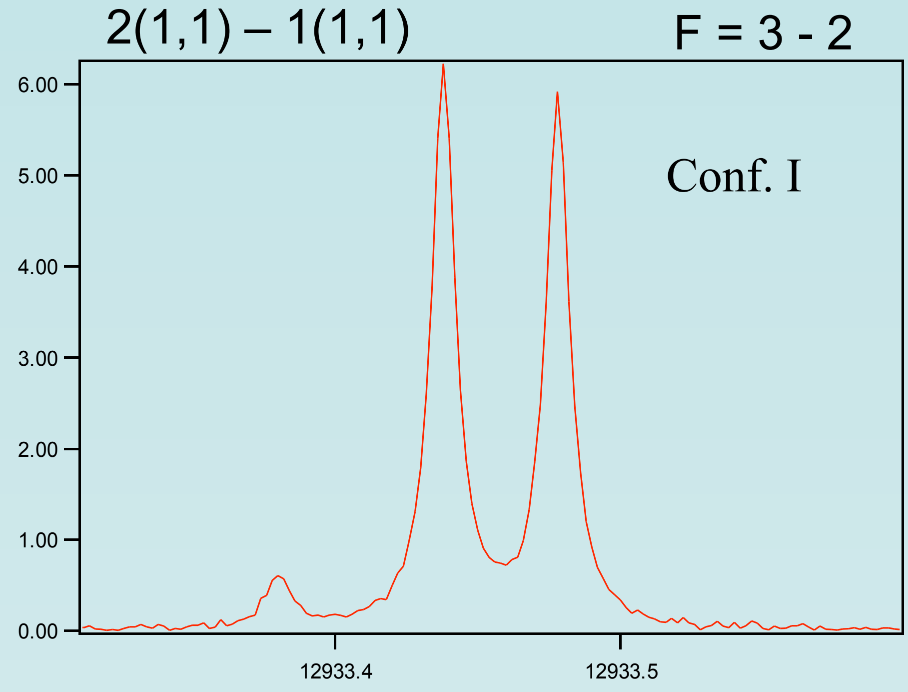
Calculated Dipole Moments

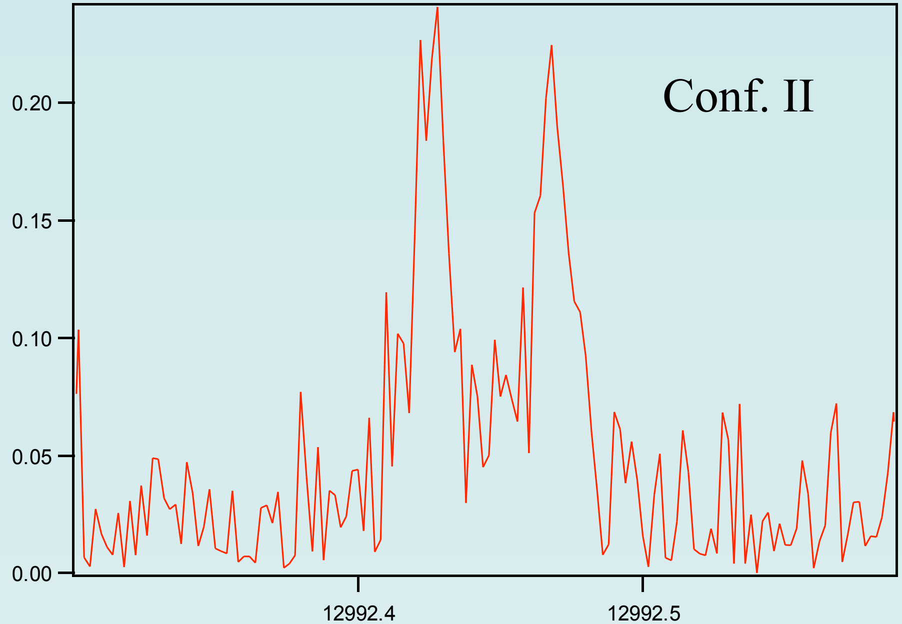
Conformer I:
μ_a = 2.32 D; μ_c = 1.67 D

Conformer II:
μ_a = 2.94 D; μ_b = 1.25 D



Conformer I vs. II





Using normal backing pressure of 40 psia conformer II signals are undetectable.

Reducing the backing pressure to about 30 in of Hg above vacuum reduced the signals of Conformer I by a factor of 20, but allowed for the detection of Conformer II signals in the microwave.

115 cm^{-1} above ground

Lactonitrile Constants

Parameter	Conformer I Experimental (MHz)	Conformer I Theoretical (MHz)	Conformer II Experimental (MHz)	Conformer II Theoretical (MHz)
A	8790.20855(106)	8816	8584.059(135)	8596
B	4005.854834(313)	3996	4028.6686(306)	3987
C	2975.800820(303)	2960	2987.8407(64)	2971
D_J	0.0009642(137)		0.0010006(296)	
D_{JK}	0.012371(74)		0.011287(37)	
D_K	-0.004083(240)		-0.00621(157)	
δ_J	-0.0002330(55)		-0.0002333(155)	
δ_K	-0.007814(126)		-0.006935(125)	
X_{aa}	-4.08723(137)		-4.053(45)	
X_{aa}-X_{bb}	0.51196(280)		0.300(20)	
μ – wave RMS	0.0015		0.005	
mm-wave RMS	0.084		0.031	

Acknowledgements

- Thanks to Jens Grabow for the help getting the FTMW++ software running
- Thanks to Isabella Kleiner for the Rho-axis code