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Millimeter/Submillimeter Detection of Methanol Clusters in a Supersonic Expansion Source

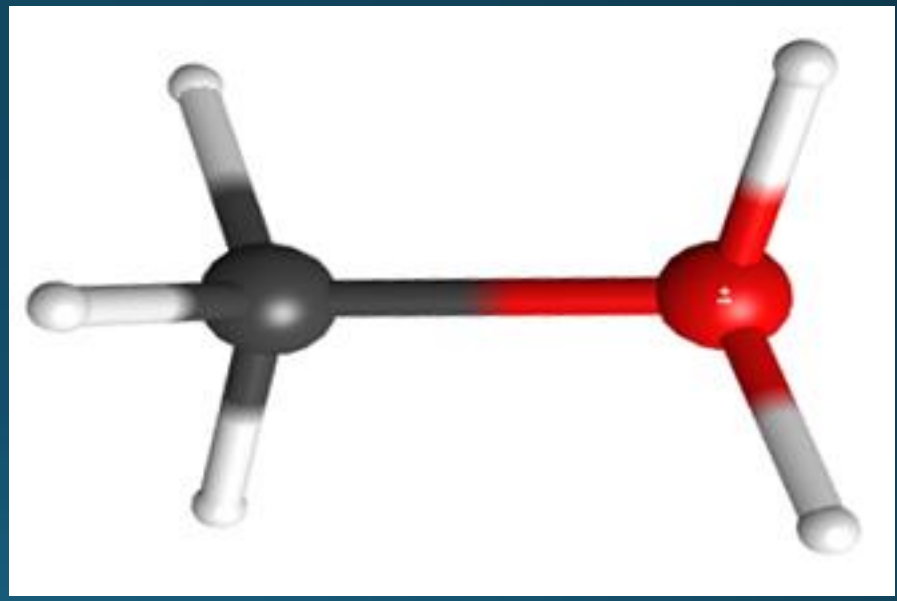
The Interstellar Medium

- Diffuse Clouds:
  - Molecular density: 100-500 molecules/cm^3
  - Temperatures range from 30-100 K
- Dense Clouds:
  - Molecular density: 1,000+ molecules/cm^3
  - Temperatures range from 10-30 K
- Star Forming Regions:
  - Molecular density: 1,000+ molecules/cm^3
  - Temperatures range from 100-300 K

Herbst, E. Chem. Soc. Rev. 2001, 30, 168–176.
Indriolo, N.; McCall, B. J. Chem. Soc. Rev. 2013, 42, 7763–7773.
NASA, ESA, and the Hubble Heritage Team, 2014, http://hubblesite.org/news_release/news/2015-01/112-hubble-heritage

Ions in the Interstellar Medium

- Ion-Molecule reaction chemistry fuels gas-phase chemistry in the ISM
- Organic ions have low production efficiencies and weak signals
- Organic ions haven’t been studied extensively

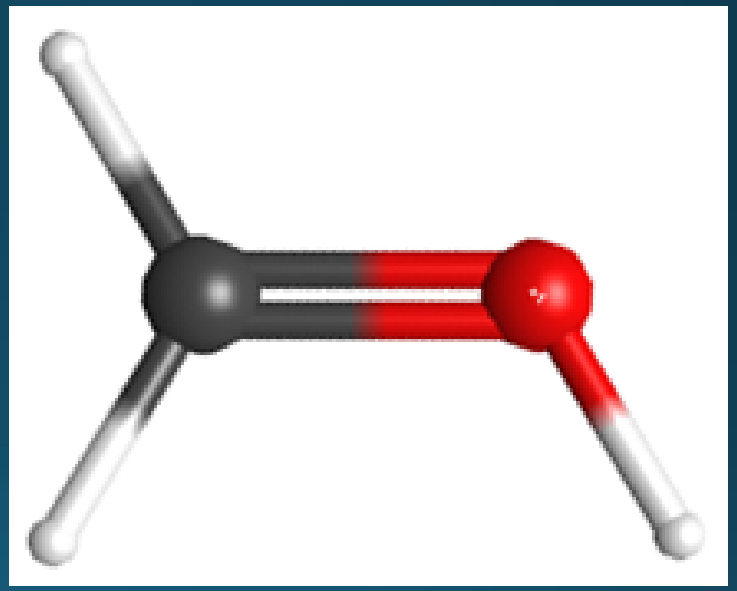


$H_3COH_2^+$

Herbst, E. Chem. Soc. Rev. 2001, 30, 168–176.
Indriolo, N.; McCall, B. J. Chem. Soc. Rev. 2013, 42, 7763–7773.

Protonated Formaldehyde

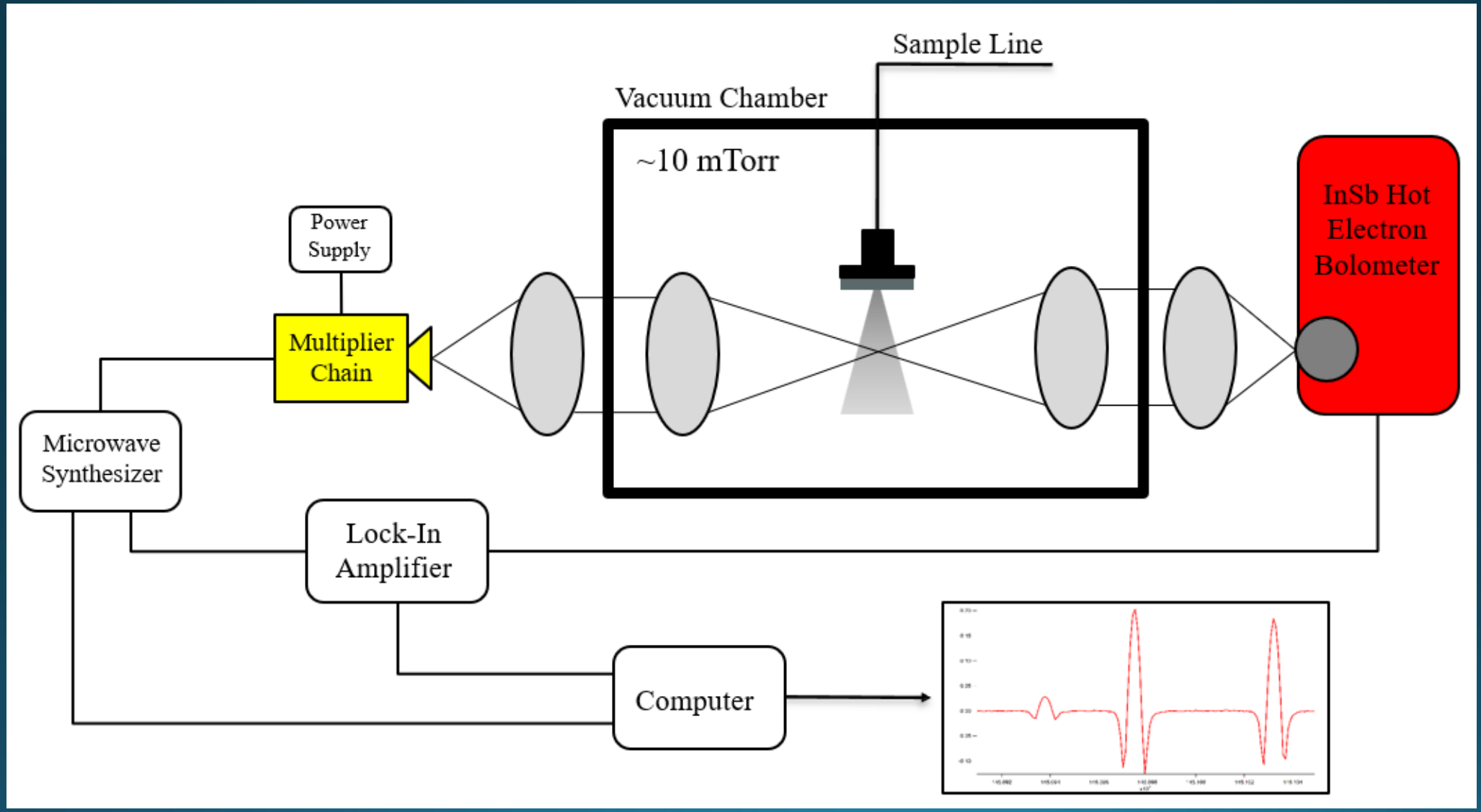
- Previously Studied: 120 – 385 GHz
- Detected in the ISM: Sgr B2, Orion KL, W51, L1689B
- Test molecule before attempting protonated methanol



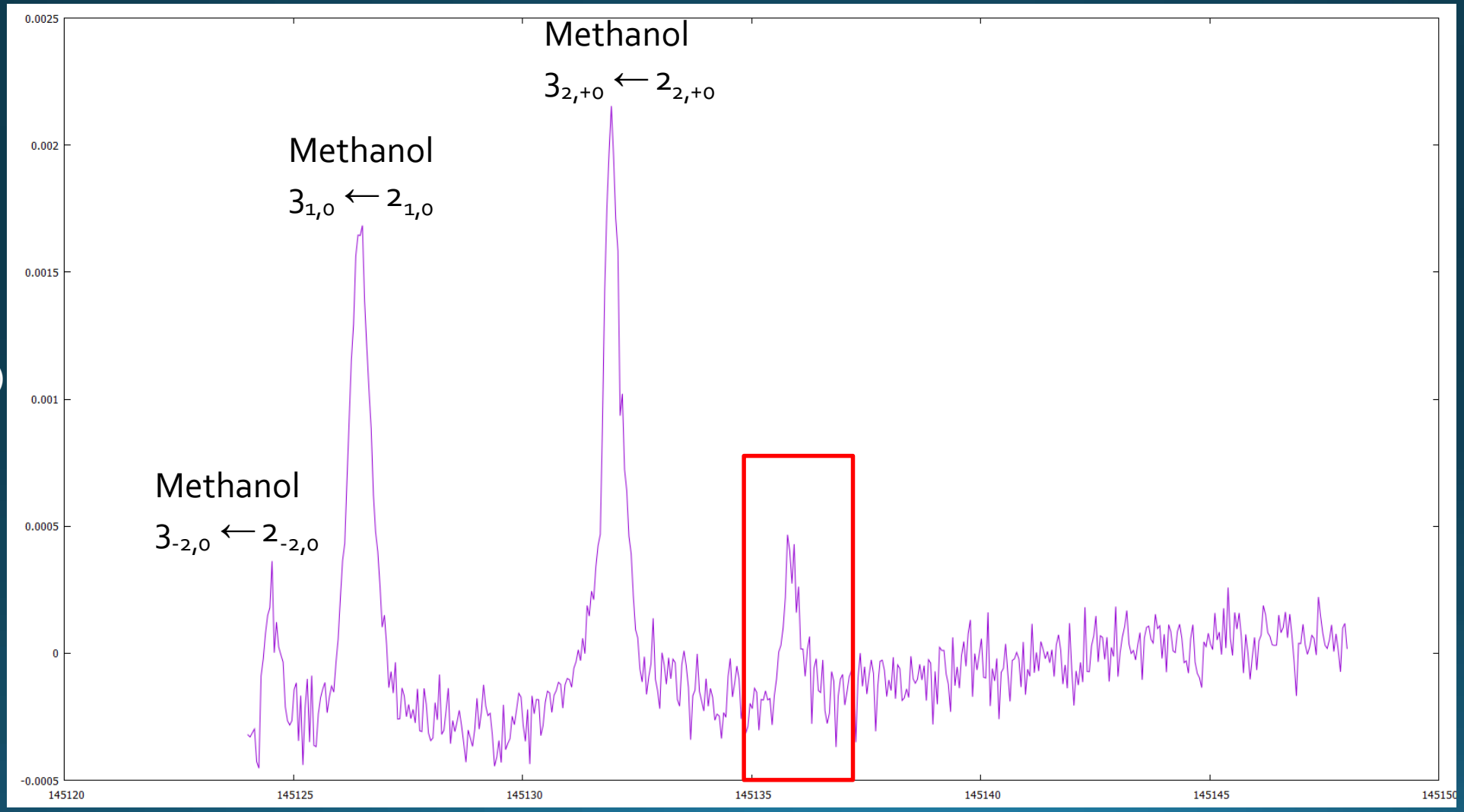
H_2COH^+

Chomiak, D.; Taleb-Bendiab, A.; Civis, S.; Amano, T. *Canadian Journal of Physics* **1994**, 72 (11-12), 1078-1081.
Dore, L.; Cazzoli, G.; Civi, S.; Scappini, F. *Chemical Physics Letters* **1995**, 244, 145-148.
Bacmann, A.; Garcia-Garcia, E.; Faure, A. A&A 2016, 588, L8.
Ohishi, M.; Ishikawa, S.-I.; Amano, T.; Oka, H.; Irvine, W. M.; Dickens, J. E.; Ziurys, L. M.; Apponi, A. J. APJL 1996, 471, L61.

Experimental Setup

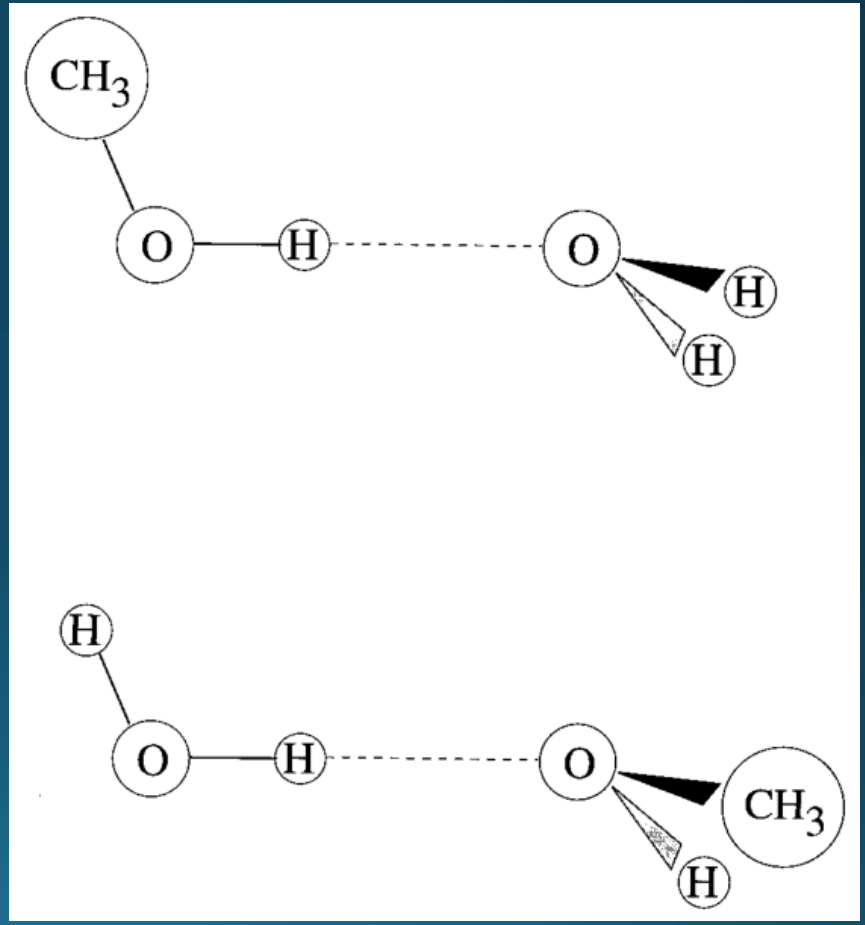


Unknown Line



Methanol Clusters

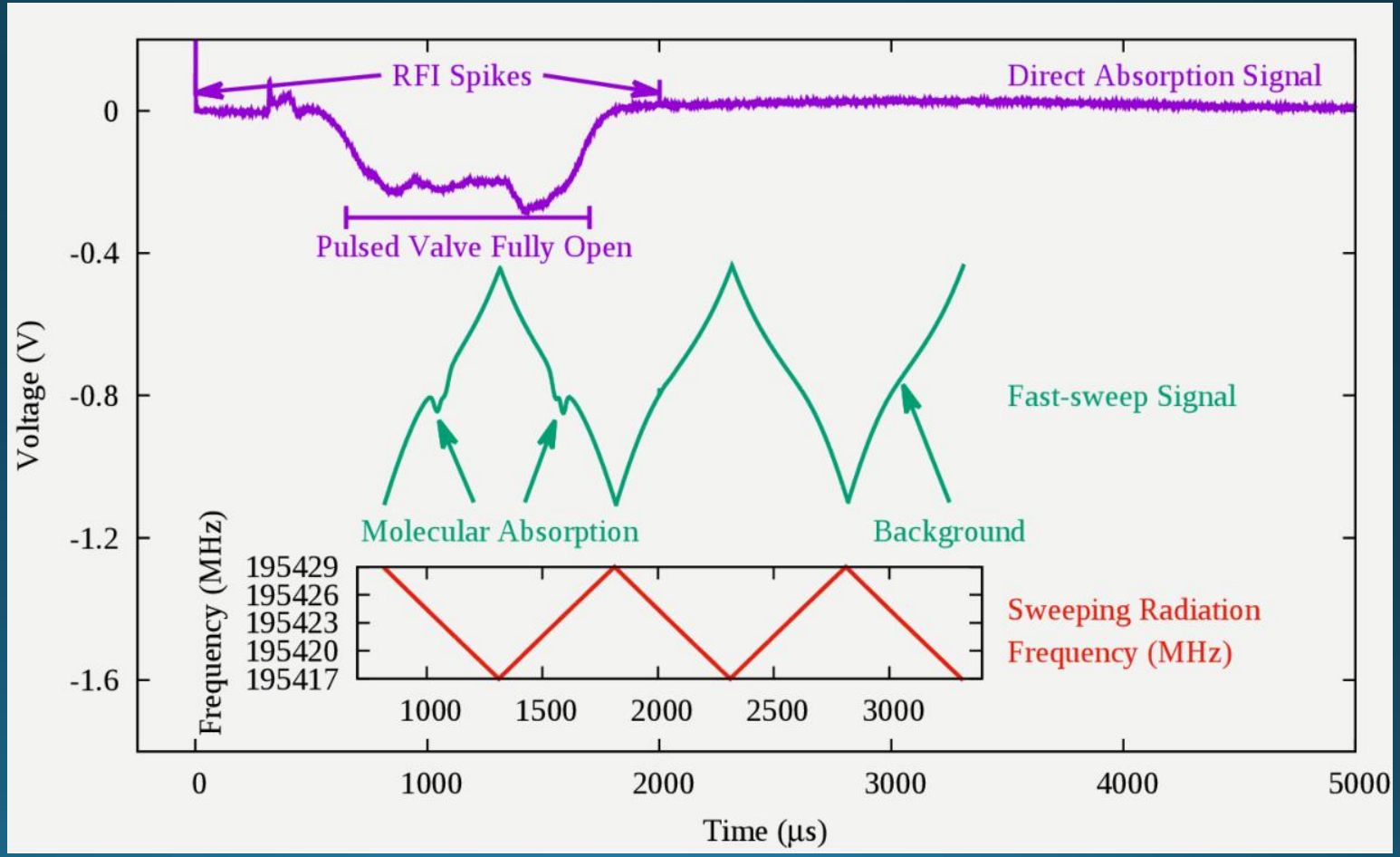
- Van der Waals
  - Methanol-Argon
- Hydrogen Bonding
  - Methanol-Water
  - Methanol Dimer



Stockman, P. A.; Blake, G. A.; Lovas, F. J.; Suenram, R. D. Journal of Chemical Physics 1997, 107, 3782-3790.

Fast Sweep Method

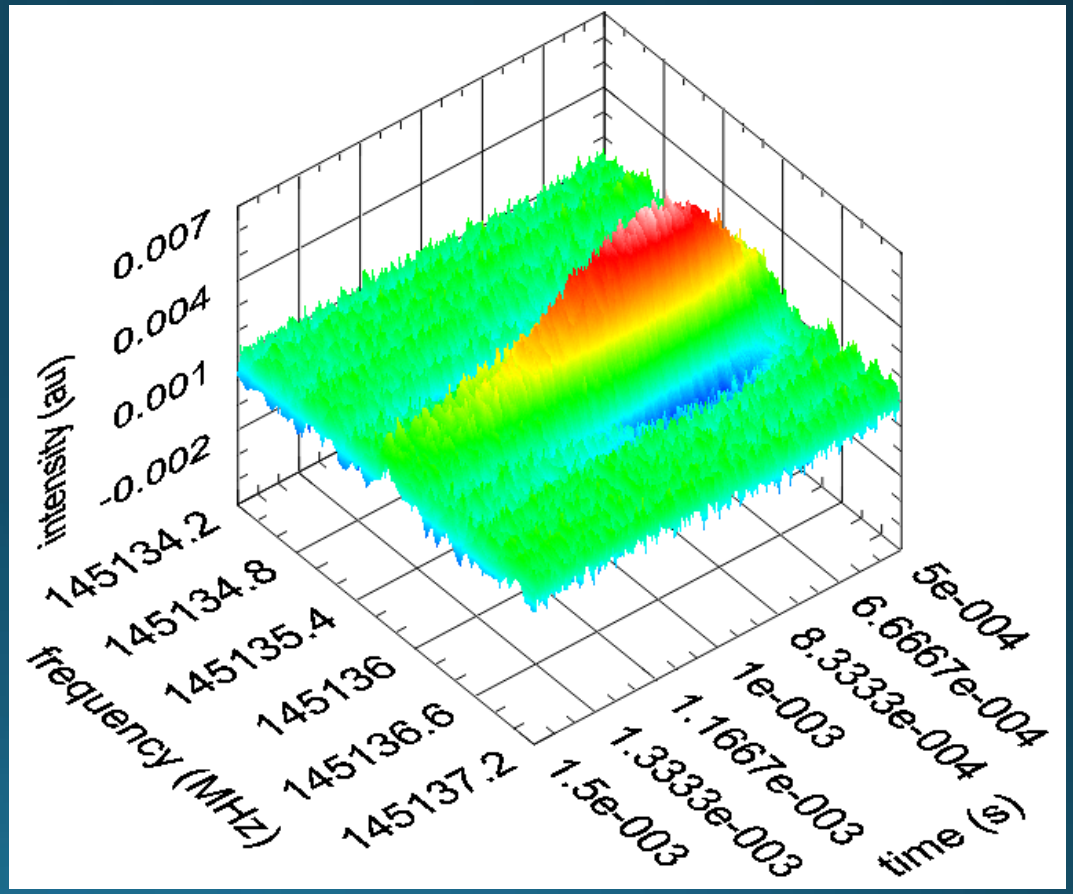
- Advantage:
  - ~100 times faster than Lock-in detection
- Disadvantages:
  - Lower sensitivity than Lock-in detection
  - Impure triangle wave



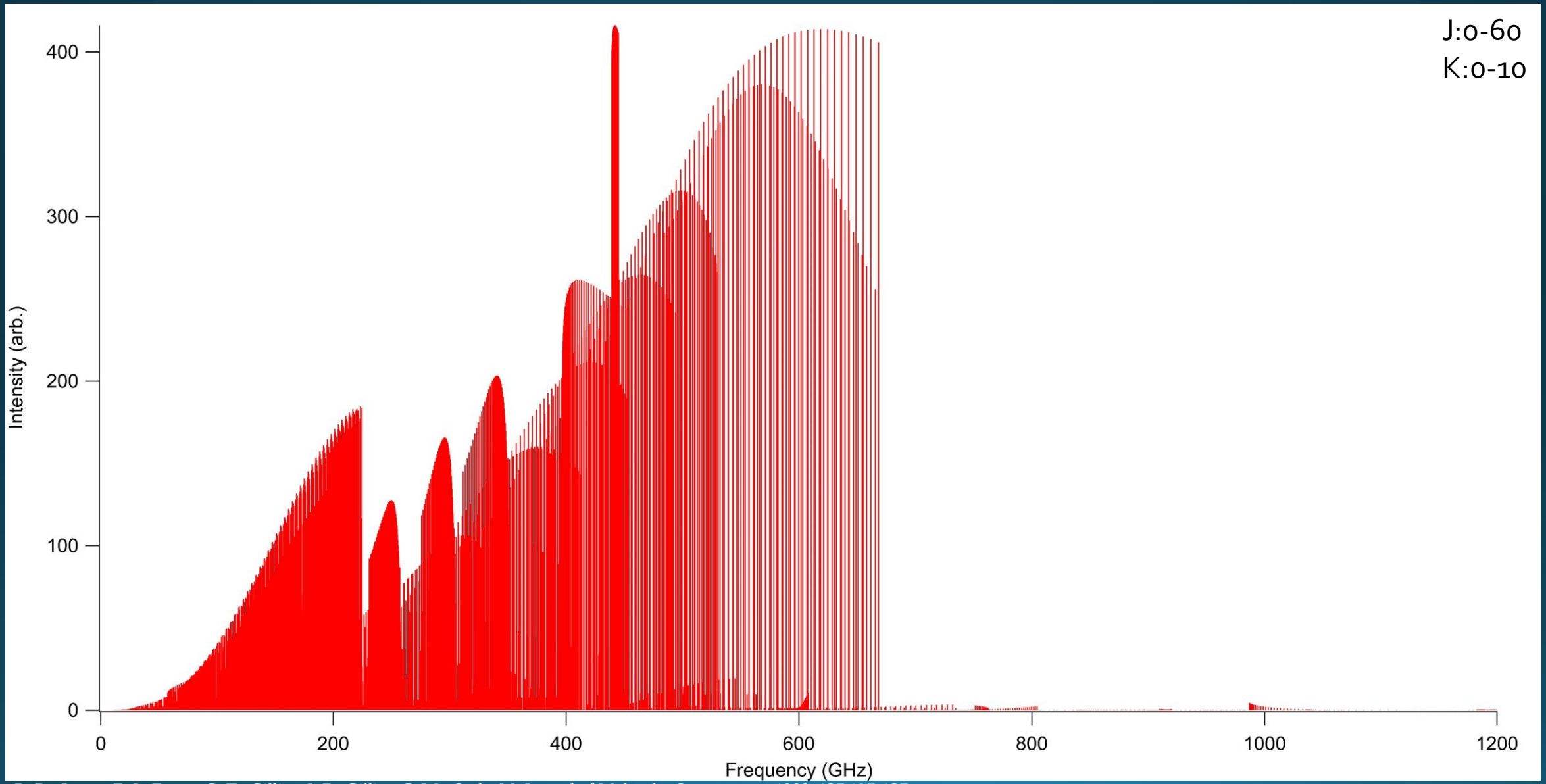
Zou, L.; Hays, B. M.; Weaver, S. L. W. The Journal of Physical Chemistry A 2016, 120, 657–667.

Pulse Valve Triggered Lock-In Detection

- Ties lock-in detection to pulse valve trigger
  - Increases duty cycle
  - Increased sensitivity of direct absorption

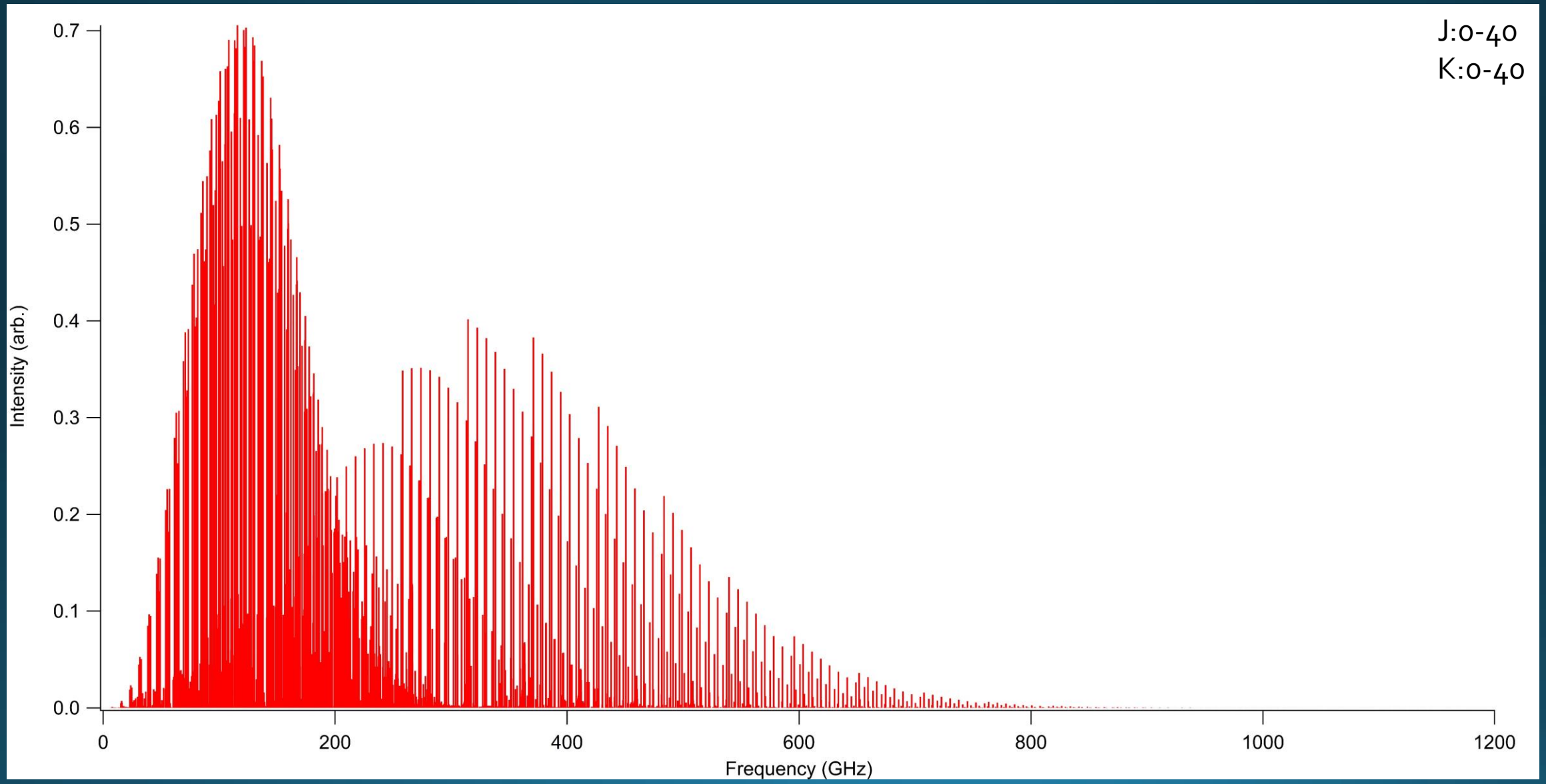


Methanol-Argon Predictions



Suenram, R. D.; Lovas, F. J.; Fraser, G. T.; Gillies, J. Z.; Gillies, C. W.; Onda, M. Journal of Molecular Spectroscopy 1989, 137,127-137.

Methanol-Water Prediction



Stockman, P. A.; Blake, G. A.; Lovas, F. J.; Suenram, R. D. Journal of Chemical Physics 1997, 107, 3782-3790.

Methanol Dimer Predictions

Rotational and Tunneling Parameters[a] (MHz) for the $K = 1$ State of $(CH_3OH)_2$

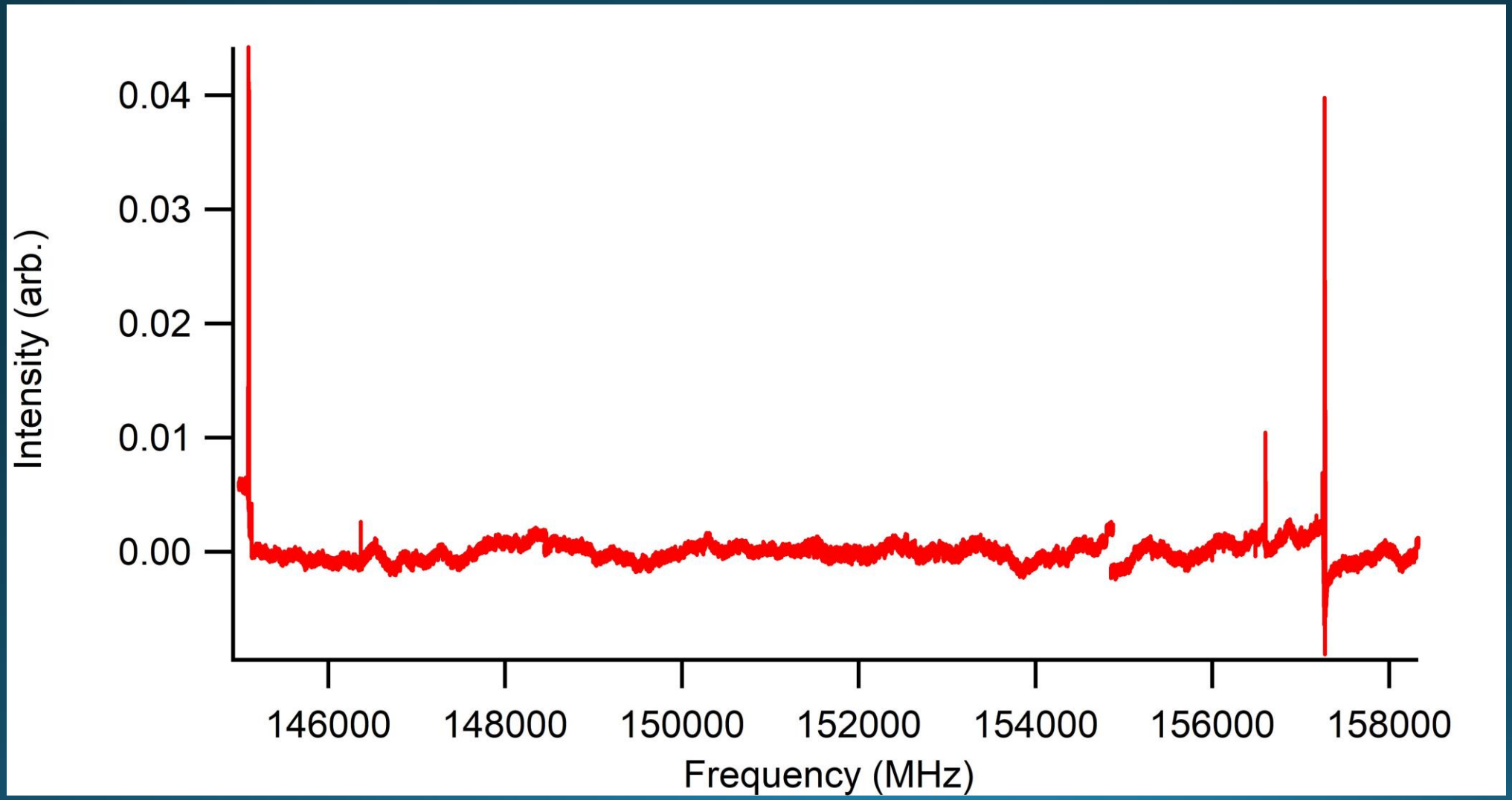
non-tunneling			
A-(B+C)/2	14312.29844(97)	D_J	0.0247524(97)
(B+C)/2	2282.77268(23)	δ_J	-0.00284(22)
B-C	43.622(43)	h_J	-0.000075(12)
CH_3 internal rotation tunneling			
$h_{3v}^r - h_{3v}(0)$	-0.04859(63)	h_{3v}^i	-0.18788(89)
h_{3j}^r	0.03881(14)	h_{3j}^i	0.01246(33)
h_{3jj}^r	-0.0003714(62)	h_{3jj}^i	0.000653(84)
$h_{7v}^r - h_{7v}(0)$	45.01599(71)	h_{7v}^i	-849.38143(86)
h_{7j}^r	0.57995(16)	h_{7j}^i	0.20070(30)
h_{7jj}^r	0.0006431(71)	h_{7jj}^i	-0.001490(70)
$h_{9v}^r - h_{9v}(0)$	0.39840(63)	h_{9v}^i	2.44959(88)
h_{9j}^r	-0.03617(15)	h_{9j}^i	0.01977(32)
h_{9jj}^r	0.0003190(62)	h_{9jj}^i	0.000519(76)
$h_{11v}^r - h_{11v}(0)$	20.77527(71)	h_{11v}^i	-304.70399(83)
h_{11j}^r	0.28863(16)	h_{11j}^i	0.05252(32)
h_{11jj}^r	-0.0000039(71)	h_{11jj}^i	-0.003791(51)

lone-pair exchange tunneling			
h_{19j}	0.15975(28)		
h_{19jj}	0.000063(15)		
h_{19v}^r	-325.21(44)	h_{19v}^i	-123.2(12)
h_{19j}^r	-0.1855(64)	h_{19j}^i	0.155(15)
h_{19jj}^r	0.00144(12)		
h_{19jjj}^r	-0.0000302(39)		
h_{21v}^r	0.10060(78)	h_{21v}^i	0.02497(81)
h_{21j}^r	-0.00640(29)	h_{21j}^i	-0.00035(19)
h_{21jj}^r	-0.000663(61)	h_{21jj}^i	-0.0000832(82)
h_{25v}^r	-30.190(38)	h_{25v}^i	-6.752(11)
h_{25j}^r	-0.02793(67)	h_{25j}^i	-0.06221(19)
h_{25jj}^r	0.001584(81)	h_{25jj}^i	0.0001987(74)
h_{25jjj}^r	-0.0000334(32)		
h_{27v}^r	-0.04639(82)	h_{27v}^i	0.04621(80)
h_{27j}^r	0.00671(24)	h_{27j}^i	-0.00158(19)
h_{27jj}^r	-0.000526(48)	h_{27jj}^i	-0.0000467(81)
h_{29v}^r	0.53373(93)	h_{29v}^i	-0.33648(84)
h_{29j}^r	-0.00439(28)	h_{29j}^i	0.03055(17)
h_{29jj}^r	-0.000704(58)	h_{29jj}^i	-0.0001350(72)
donor-acceptor exchange tunneling			
h_{2v}	-0.01204(42)	h_{14v}	-0.00391(44)
h_{12v}	-0.01282(84)	h_{36v}	-0.00328(41)

Lugez, C. L.; Lovas, F. J.; Hougen, J. T.; Ohashi, N. Journal of Molecular Spectroscopy 1999, 194, 95-112.

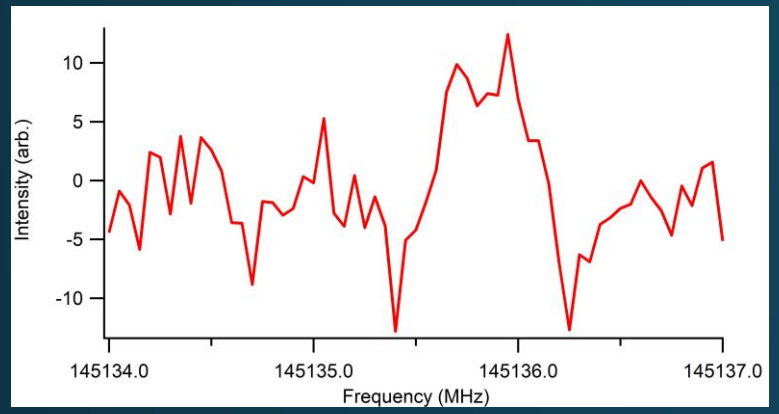
Fast Sweep Scans

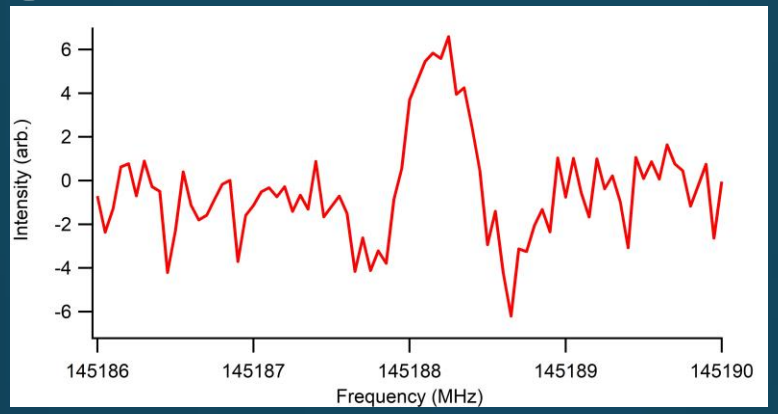
1000 avg, Resolution: 48 kHz

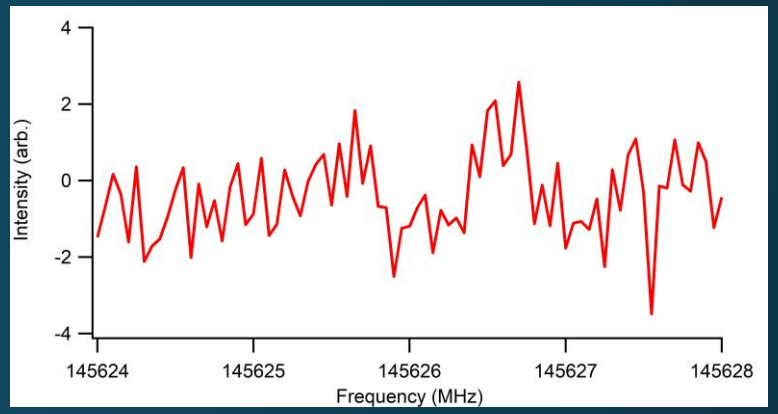


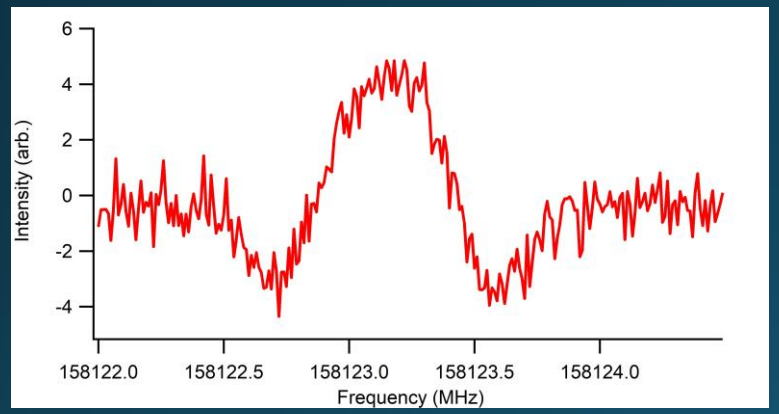
Current Unassigned lines

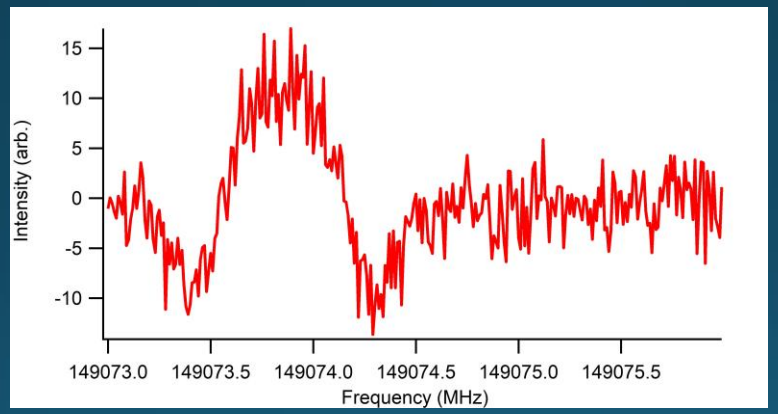
10 avg, Resolution: 50 kHz

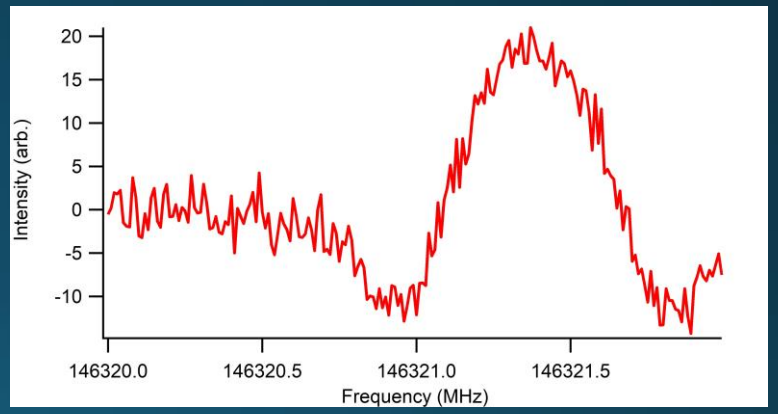




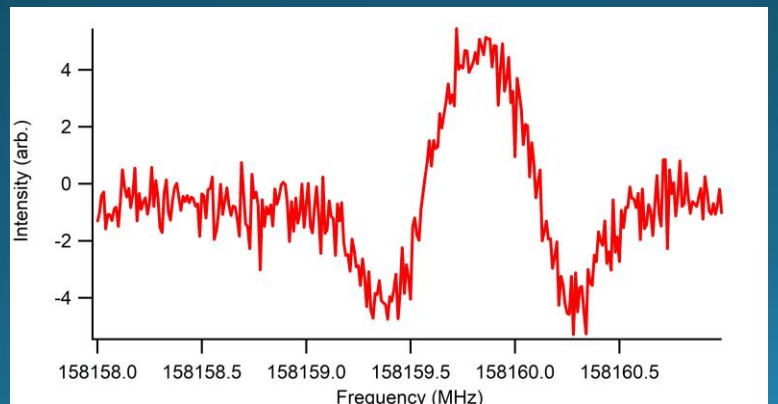








10 avg, Resolution: 10 kHz



Future Direction

- Expand our use of pulse valve triggered lock-in detection
  - Demonstrate lock-in fast sweep
- Use the methanol cluster spectrum to clean up future spectra
  - Help to determine new unknown lines from old previously assigned lines
  - Should prove useful in assigning protonated formaldehyde and protonated methanol

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Questions?