AIR-BROADENED LINE SHAPES IN THE $2\nu_3$ R BRANCH OF $^{12}CH_4$ BETWEEN 6014 AND 6100 cm^{-1}

V. Malathy Devi & D. Chris Benner

Department of Physics, The College of William and Mary

K. Sung, L.R. Brown, T.J. Crawford. Shanshan Yu

Jet Propulsion Laboratory, California Institute of Technology

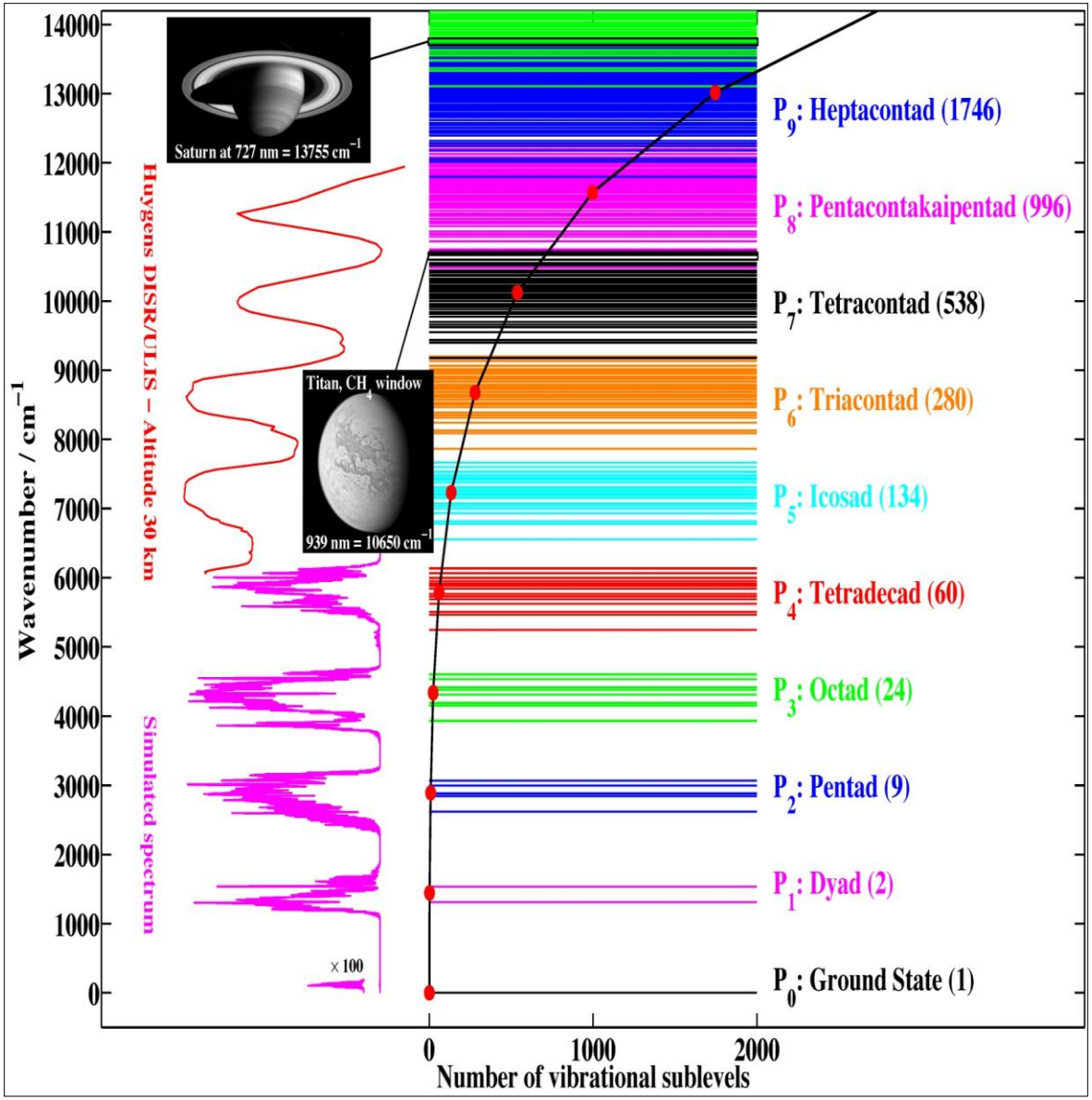
M.A.H. Smith

Science Directorate, NASA Langley Research Center

A.W. Mantz

Department of Physics, Astronomy and Geophysics, Connecticut College

VIBRATIONAL ENERY LEVELS IN METHANE POLYAD



This highly informative and extremely beautiful figure illustrating the various vibrational energy levels in methane has been cited in several papers, oral and poster presentations

We thank Dr. Vincent Boudon for allowing us to show this diagram at this talk

$2\nu_3$ is one of the 14 interacting vibrational bands appearing in the Tetradecad Polyad with 60 sublevels (as shown in red on left, around 6000 cm^{-1})

Goals and brief details of the present measurements

1. Systematic biases in the methane concentration retrievals are thought to be introduced by improper characterization of laboratory spectra.
2. The main goal in this study was to obtain complete and accurate information on line shape parameters of $2\nu_3$ transitions for air- (and self-) broadening vs. temperature to support atmospheric remote sensing studies and obtain total column CH_4 measurements with sub-1% accuracies.
3. The Q and R branch spectral regions (~5980-6140 cm^{-1}) in this band are most commonly used for methane retrievals (e.g. for SCIAMACHY, GOSAT…).
4. However, accurate measurements in the Q and R branches are extremely difficult and challenging because of severe blending of absorption features in the various manifolds.
5. Analysis software capable of measuring line shape phenomena such as collisional narrowing, line mixing, and speed dependence (in addition to usual line parameters) is critical to fit the laboratory data. Consistent & accurate results will help develop a reliable theoretical model.
6. Present study represents the FIRST experimental measurements of air-broadening and also self- and air-broadened off-diagonal relaxation matrix elements in the R0-R9 manifolds involved in line mixing and measured or estimated T-dependences for both broadening cases.
7. A multispectrum nonlinear least squares curve fitting technique modified to include speed dependent Voigt profile and full line mixing using the off-diagonal relaxation matrix element formalism has been applied to fit 25 laboratory spectra obtained at (JPL) at various temperatures and gas pressures.

The following topics will be briefly discussed during this presentation

1. Objective
2. Prior Studies in this spectral region
3. Experimental Details
4. Sample spectra
5. Analysis technique
6. Instrumental line shape effects
7. Sample multispectrum fits of a few R-branch manifolds
8. Auxiliary parameters and constraints, a few examples will be shown
9. Examples of Line mixing using the off-diagonal relaxation matrix formalism
10. Results; e.g. Positional and Intensity comparisons with other recent measurements
11. Future plans
12. Summary and Conclusions
13. Acknowledgments

DATA RETRIEVAL DETAILS

- A total of 25 spectra, recorded at room temperature and cold temperatures, as well as self- and air-broadened were fitted simultaneously, but separately for each manifold applying a multispectrum nonlinear least squares spectrum fitting technique [1]. Examples of fits will be shown.
- A speed-dependent Voigt profile was assumed. For specific pairs of lines in a manifold, line mixing (both self- air-) was necessary to fit the spectra within the noise level.
- Spectral backgrounds, zero transmission levels, FTS phase error, and FTS instrument function (such as the field of view correction) were appropriately modeled. Some problems still remain.
- Initial values for line parameters were taken from HITRAN2012 database linelist.
- Position calibration: Relative wavenumber scales were first calibrated with respect to positions of 2←0 band of HCl lines. Absolute calibration is currently performed w.r.t the R0 line position from Ishibashi et al. [2] rather than Zolot et al. [3] as was initially thought. Will discuss why.
- Parameters measured: Line position, intensity, air- and self-broadened width coefficients and their T-dependences, air- and self- pressure-shift coefficients and their T-dependences, where appropriate line mixing (off-diagonal relaxation matrix) and T-dependence of line mixing (measured or fixed) and speed dependence (only specific transitions). Dicke narrowing was measured for R0 and R1.

[1]. D.C. Benner et al. J Quant Spectrosc Radiat Transfer 53 (1995) 705; expanded extensively with new capabilities added in 2012 and additional features being added currently. {Multispectrum fitting technique}
[2]. C. Ishibashi et al. Optics communications, 161 (1999) 223-226. {Absolute frequency measurement of the saturated absorption lines, R0 and Q1 in the $2\nu_3$ CH_4}
[3]. A.M. Zolot et al. J Quant Spectrosc Radiat Transfer 118 (2013) 26-39. {Broad band frequency references…dual comb spectroscopy of methane and acetylene}

A number of investigators in the past have studied the shapes of $2\nu_3$ transitions using different approaches; experimental and theoretical. The most recent studies include:

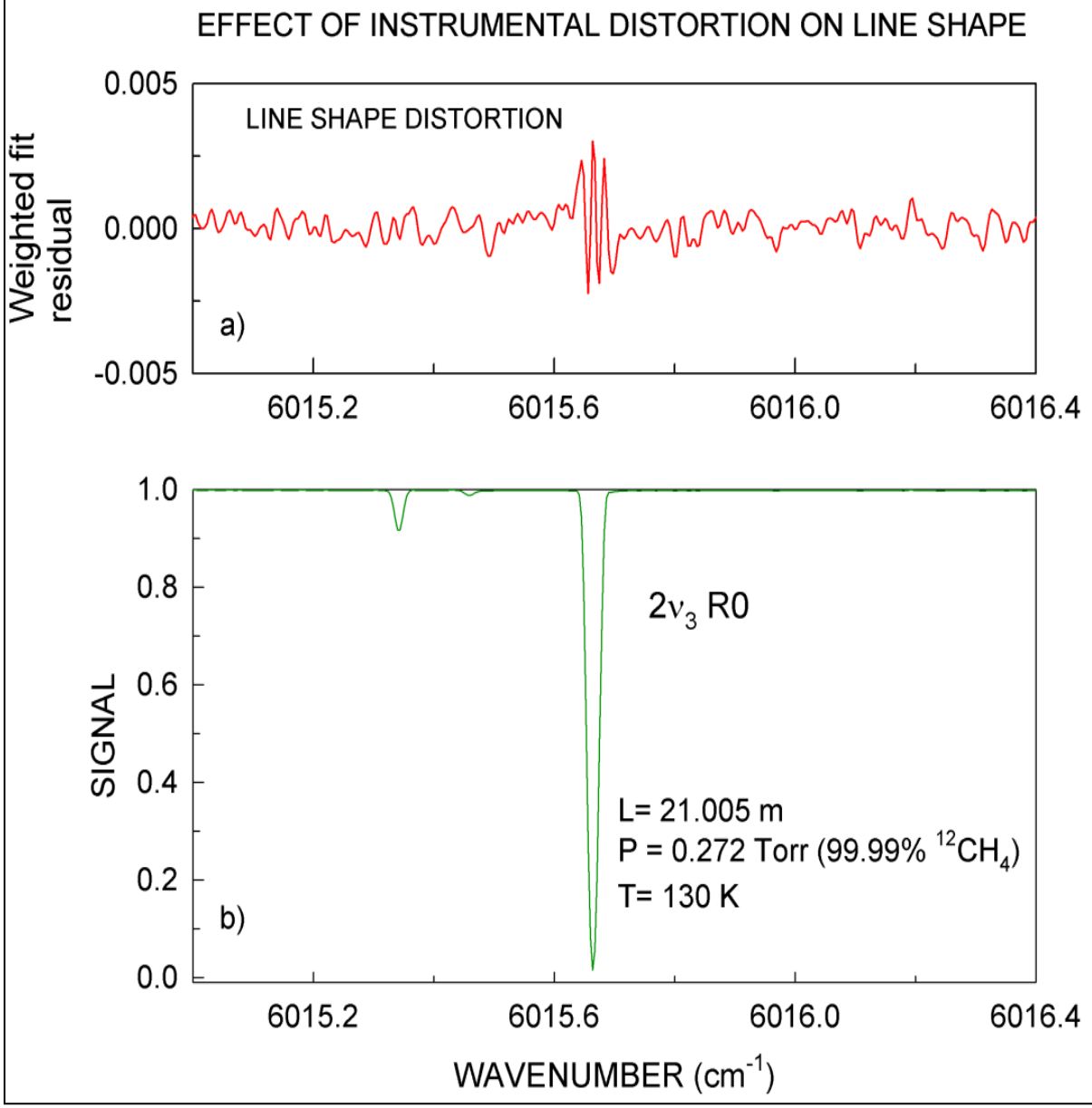
1. Kapitanov et al: Measured 2 close lying lines in the R9 manifold using PAS for N_2 and He broadening. J Mol Spectroscopy, doi.org/10.1016/jms.2013.03.009
2. Kapitanov et al. Parameters for 11 N_2-broadened lines in the R9 manifold using PAS. J Quant Spectrosc Radiat Transfer, 113 (2012) 1985-1992. Also studied the R3 multiplet in 2007.
3. Lyulin et al.: Self-broadened widths and shifts for over 400 lines in the 5556-6166 cm^{-1} from FTS spectra at 3 different temperatures. J Quant Spectrosc Radiat Transfer, 112 (2011)531-539.
4. Tran et al. N_2 broadened P & R manifolds near 6000 cm^{-1}. Analyzed HR laboratory and atmospheric spectra. Line mixing in the manifolds measured. J Quant Spectrosc Radiat Transfer, 111 (2010) 1344-1356.
5. Nikitin et al. A detailed experimental measurements in the 5550-6236 cm^{-1} from FTS data for the GOSAT mission. J Quant Spectrosc Radiat Transfer, 111 (2010) 2211-2224.
6. Lyulin et al. N_2- and O_2 broadening and shift parameters for over 450 lines at different temperatures and pressures in the 5550-6236 cm^{-1}. J Quant Spectrosc Radiat Transfer, 110 (2010) 664-668.
7. Frankenberg et al. Effective set of spectroscopic line parameters in the 5860-6185 cm^{-1} from N_2-broadened FTS data at RT and applied to atmospheric retrievals. Atmos. Chem. Phys. 8 (2008) 5061-5075.
8. Gharavi and Buckley: CO_2, N_2, H_2O, CH_4 and CO broadening in R3 and R4 using diode laser data. J Mol Spectrosc 229 (2005) 78-88.
9. Dufour et al. N_2, O_2, Ar and He-broadened line profile studies using diode laser data. J Mol Spectrosc 221 (2003) 80-92. Collisional narrowing in R0 and line mixing R3 manifold from diode laser data were also reported .

Summary of Experimental Conditions of spectra analyzed

Serial #	Spectrum Name	Path (m)	Pressure (Torr)	Volume Mixing Ratio	Temp. (C)	Zero level	Phase error
1	kp3697.aus	13.09[a]	2.57	1.0	20.95	-0.00449	359.8681
2	kp3905.aus	0.2038	100.4	1.0	24.75	-0.00567	359.8095
3	kp3903.aus	0.2038	299.2	1.0	24.75	-0.00520	359.9193
4	kp3908.aus	0.2038	499.9	1.0	-23.05	-0.00131	0.0033
5	kp3910.aus	0.2038	244.1	1.0	-23.05	-0.00270	359.9034
6	kp3912.aus	0.2038	56.8	1.0	-23.05	-0.00384	359.7215
7	kp3915.aus	0.2038	599.0	1.0	-72.95	-0.00031	0.0907
8	kp3917.aus	0.2038	138.0	1.0	-72.95	-0.00185	359.8673
9	kp3920.aus	0.2038	356.40	1.0	-122.75	-0.00105	0.1394
10	kp3922.aus	0.2038	201.5	1.0	-122.75	-0.00186	0.0362
11	kp3924.aus	0.2038	38.58	1.0	-122.75	-0.00461	359.7857
12	kp3725.aus	21.005	0.272	1.0	-143.15	-0.00175	359.7586
13	kp3742.aus	21.005	0.399	1.0	-25.05	-0.00137	0.0
14	**kp3746.aus**	**21.005**	**150.04**	**0.003678**	**-25.05**	**0.00079**	**359.9534**
14	**kp3744.aus**	**21.005**	**305.75**	**0.003710**	**-25.05**	**0.00273**	**0.0793**
15	**kp3727.aus**	**21.005**	**149.02**	**0.001820**	**-143.25**	**0.00197**	**359.9477**
17	**kp3729.aus**	**21.005**	**79.64**	**0.001820**	**-143.25**	**0.00302**	**359.8482**
18	**kp3732.aus**	**21.005**	**291.75**	**0.002380**	**-103.15**	**0.00216**	**0.1276**
19	**kp3734.aus**	**21.005**	**101.05**	**0.002410**	**-103.15**	**0.00267**	**0.0835**
20	**kp3737.aus**	**21.005**	**255.69**	**0.00292**	**-62.95**	**0.00297**	**0.2279**
21	**kp3739.aus**	**21.005**	**149.64**	**0.00290**	**-62.95**	**0.00176**	**0.0874**
22	**kp3698.aus**	**13.09[a]**	**249.95**	**0.01028**	**20.95**	**-0.00017**	**359.8531**
23	**kp3699.aus**	**13.09[a]**	**393.47**	**0.006510**	**20.75**	**0.00011**	**359.8685**
24	**kp3700.aus**	**13.09[a]**	**547.74**	**0.004680**	**20.85**	**0.00050**	**359.8671**
25	**kp3701.aus**	**13.09[a]**	**805.30**	**0.003170**	**20.85**	**-0.00039**	**359.8581**

[a] Purity of gas sample was 99.95% ^{12}C-enriched; all others had 99.99% ^{12}C-enrichment

Instrumental Line Shape Distortion

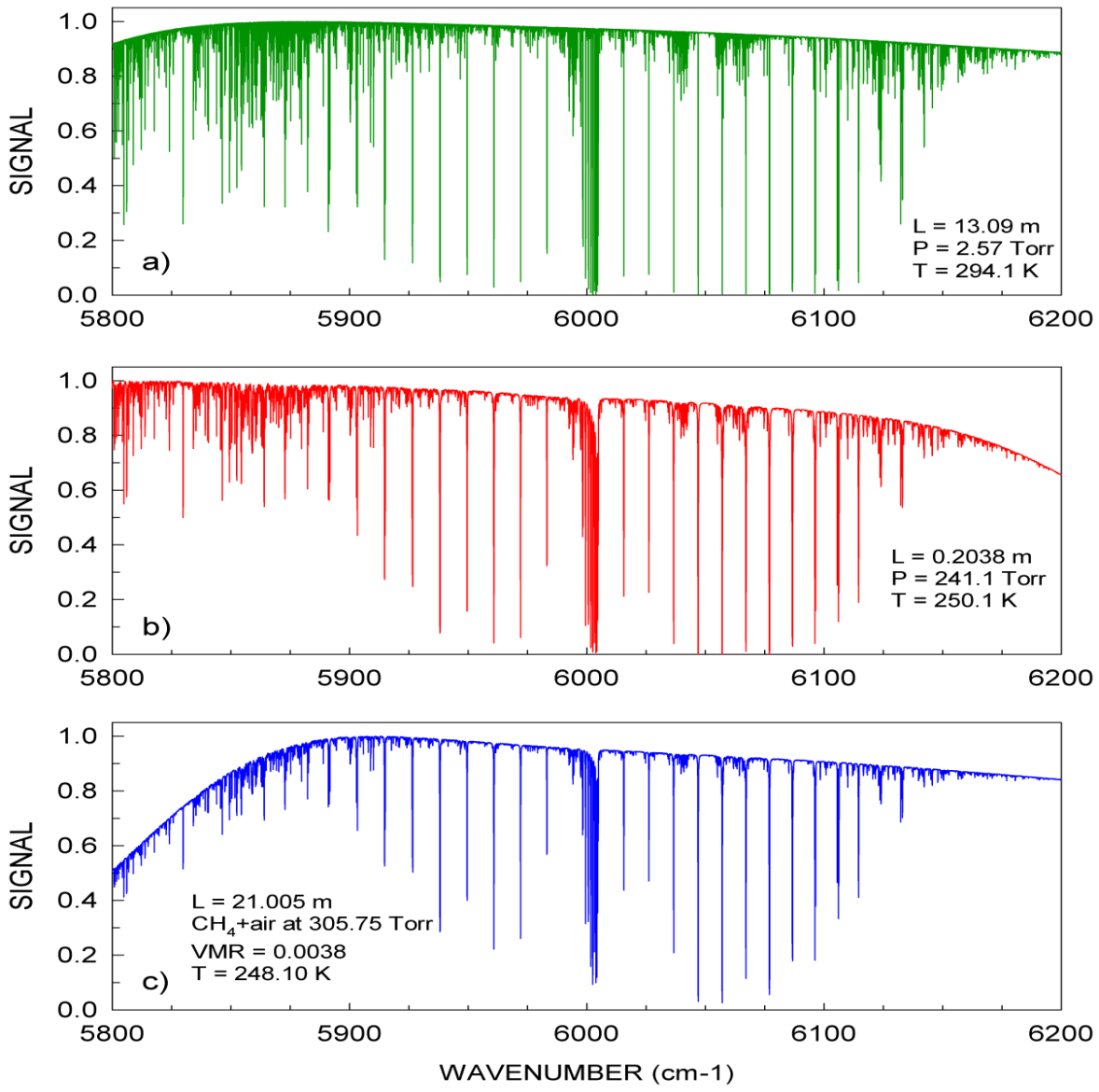


Line shape distortion such as seen in Fig. left occurs commonly in high resolution Bruker FTS spectra

Such distortions are prominent especially in low pressure spectra

Although its effects are usually small (~0.25% as seen here) it can be higher (>0.5%) and may affect the accuracy of measured parameter values at least to that amount, if not more, due to uncertainties in other physical parameters

Example spectra used in the present analysis



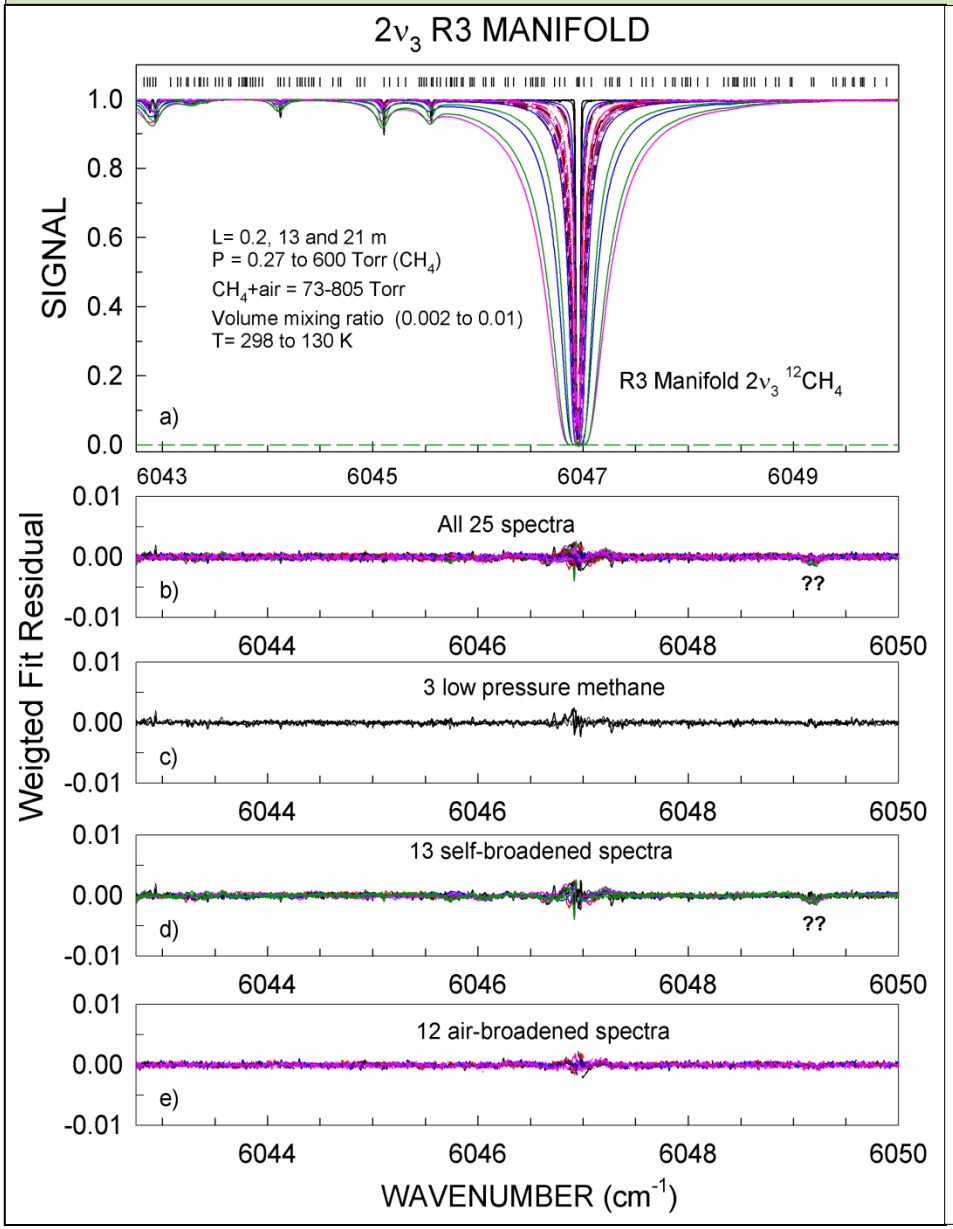
Three of the 25 spectra analyzed in this work are illustrated on the left

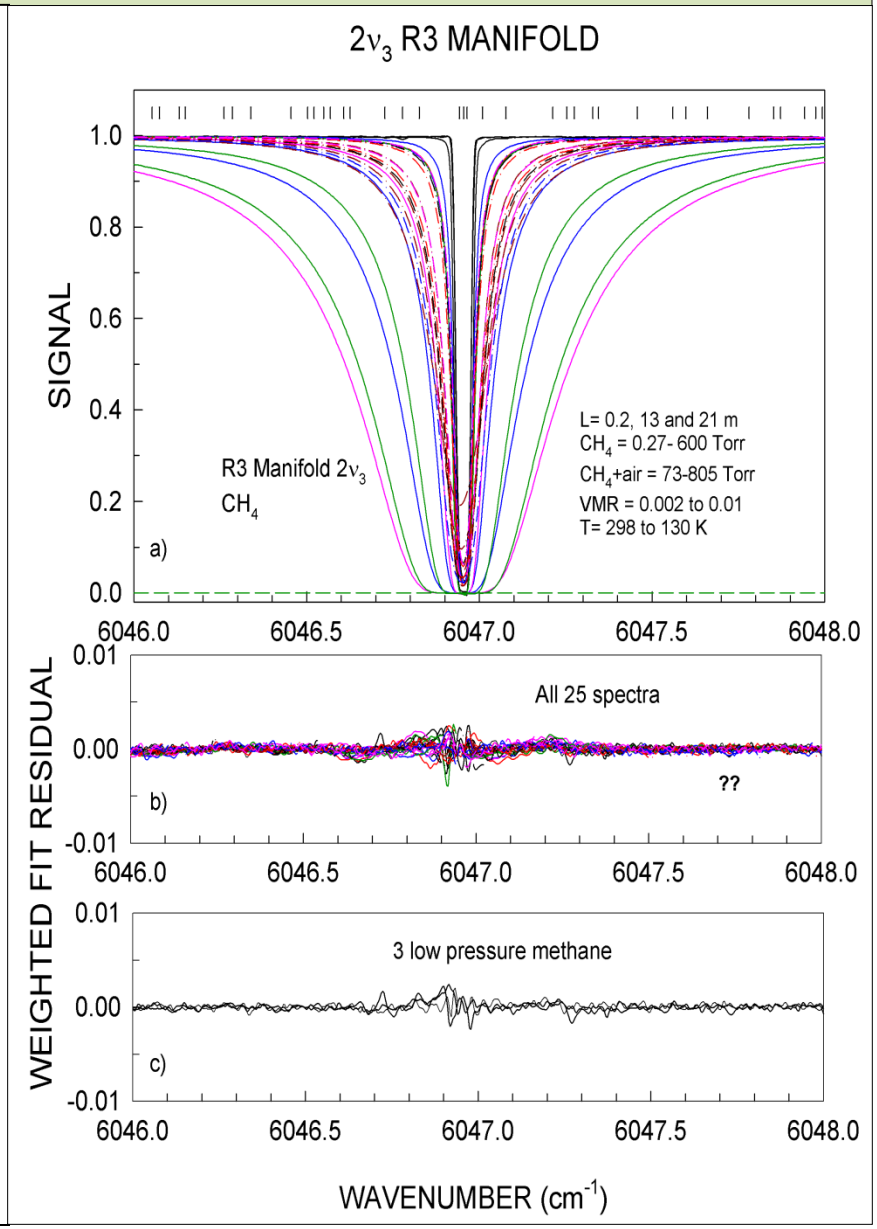
a) The spectrum at top has 2.57 Torr pure CH_4 in a 13.09 m path at 294.1 K

b) The middle spectrum has 241.1 Torr pure CH_4 in a 0.204 m cell cooled to 250. 1K

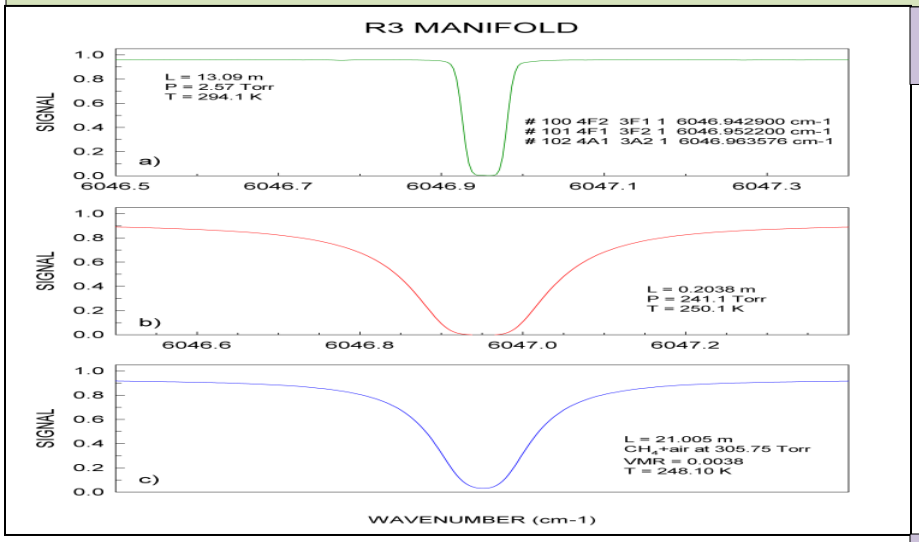
c) The bottom panel shows an air-broadened spectrum recorded using a 21.005 m path cell filled to a total pressure of 305.75 Torr at 248.1 K with a VMR of CH_4 of 0.0038

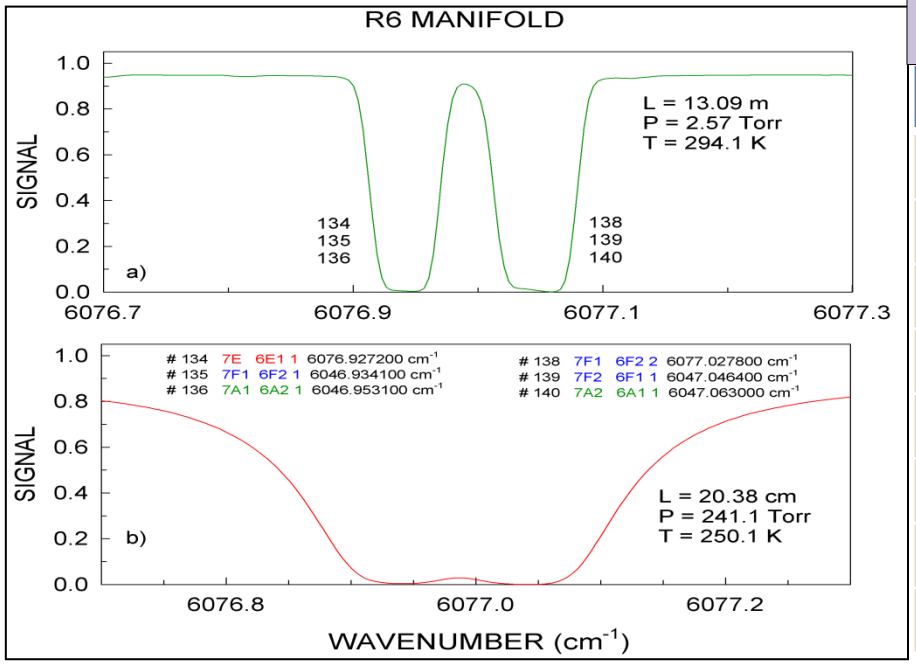
Multispectrum fits for the R3 manifold





Examples of Auxiliary Parameters used in the present analysis





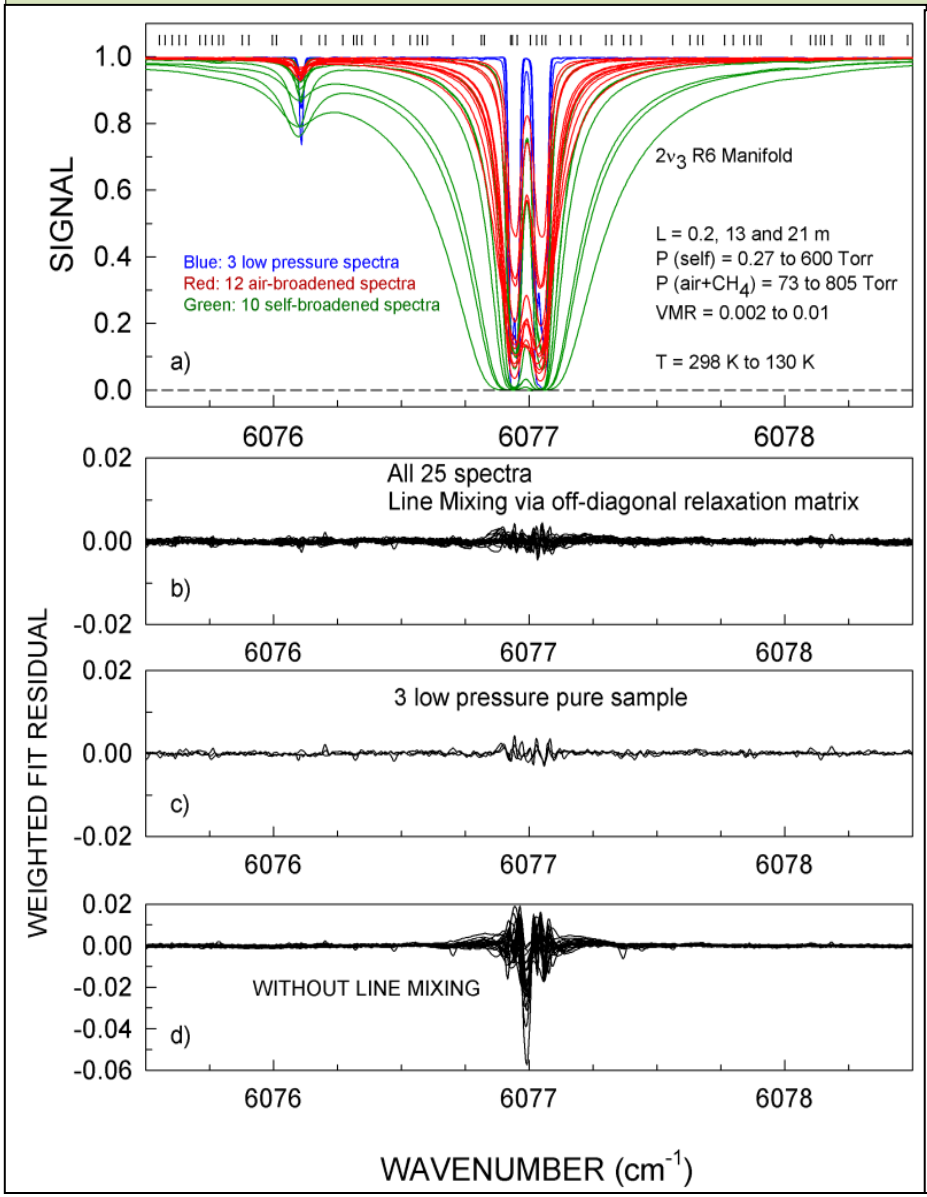
Auxiliary parameters for R3

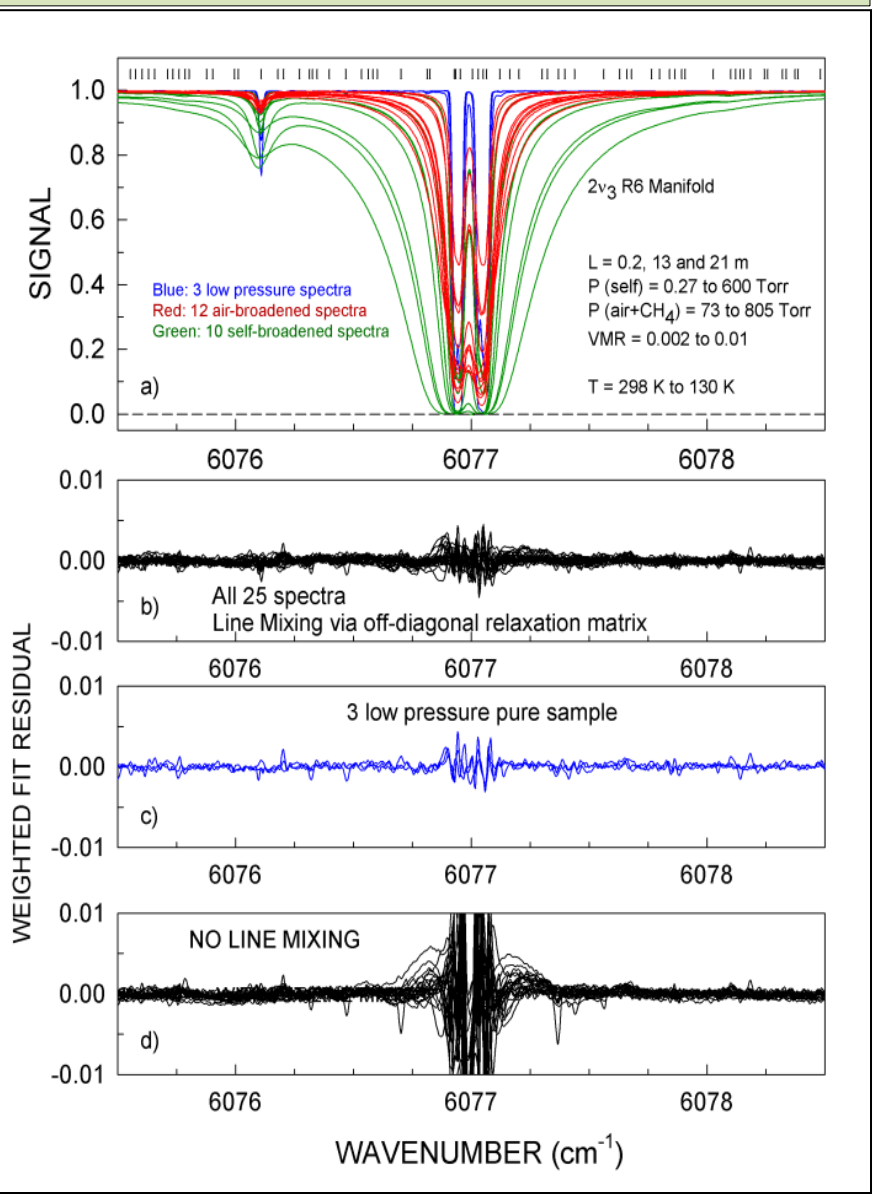
Description	[PS]	Database
Δν (101-100)	0.010679 (21) cm^{-1}	0.0093 cm^{-1}
Δν (102-100)	0.021487 (4) cm^{-1}	0.0207 cm^{-1}
Int. ratio (101/100)	0.99901(1)	1.0
Int. ratio (102 /100)	1.5722 (11)	1.785

Auxiliary parameters for R6

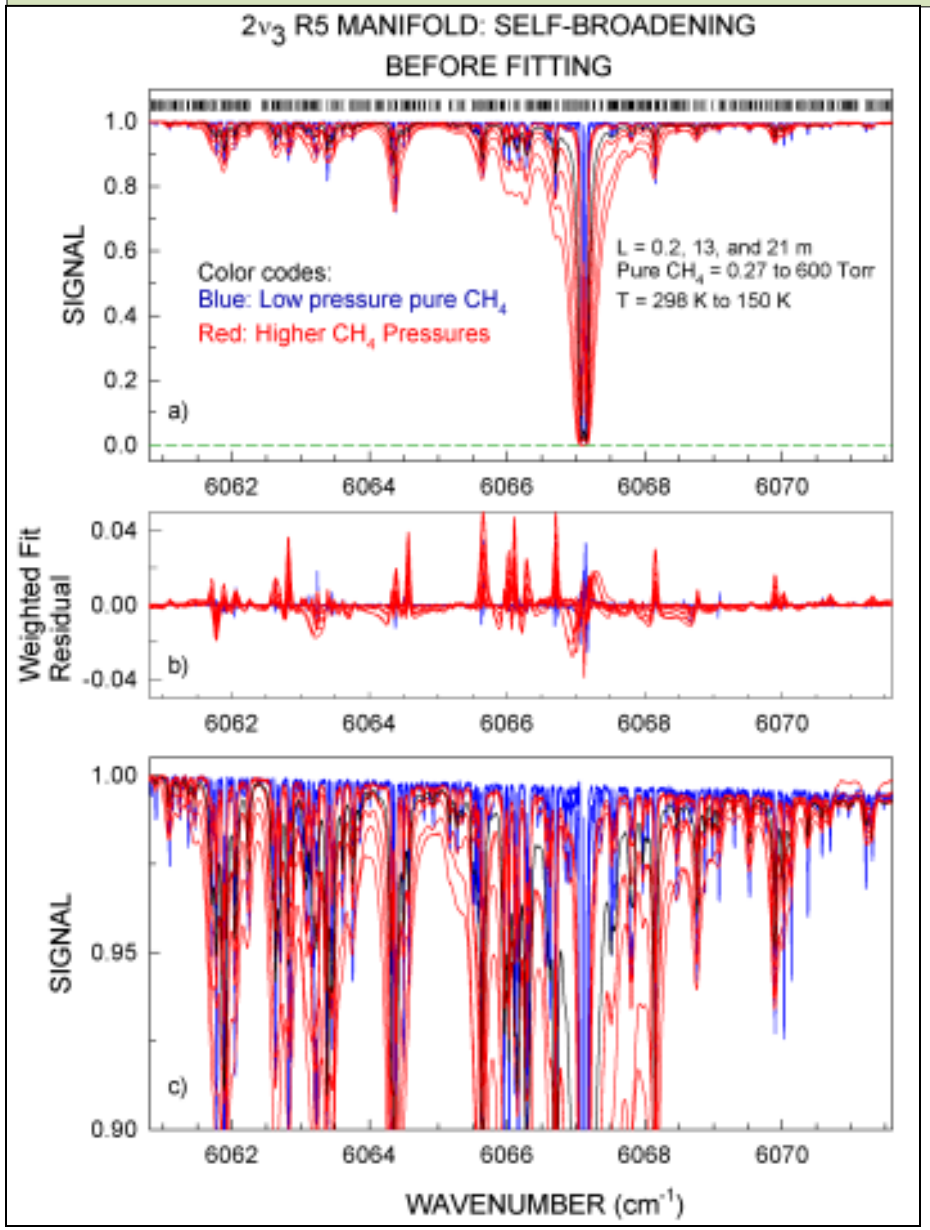
Description	[PS]	Database
Δν (135-134)	0.0068 cm^{-1} (Fixed)	0.0069 cm^{-1}
Int. ratio (135/134)	1.61 (Fixed)	1.61
Δν (136-134)	0.025641 (4) cm^{-1}	0.0259 cm^{-1}
Int. ratio (136/134)	2.6213 (6)	2.657
Δν (139-138)	0.018518 (7) cm^{-1}	0.0229 cm^{-1}
Int. ratio (139/138)	0.98226 (29)	0.9533
Δν (140-138)	0.034950 (4) cm^{-1}	0.0352 cm^{-1}
Int. ratio (140/138)	1.6317 (3)	1.633

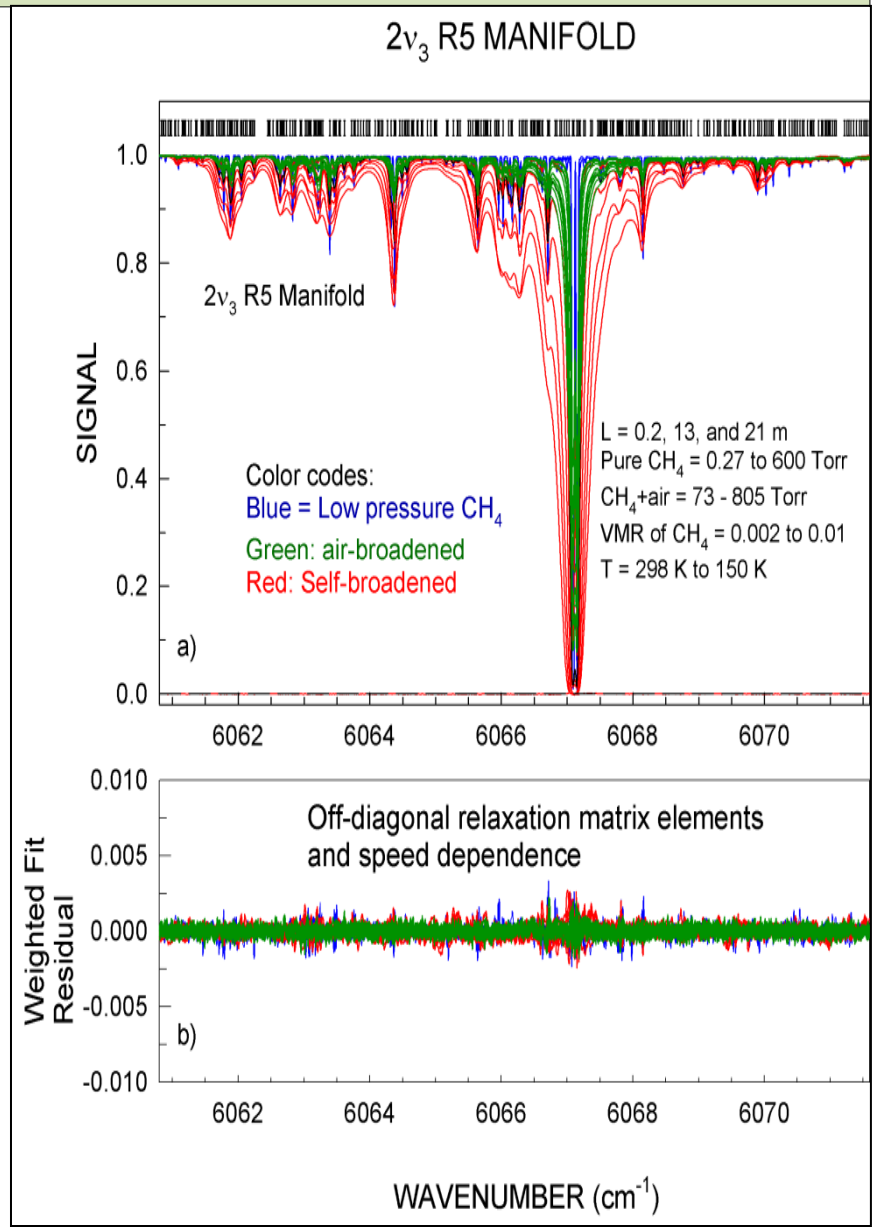
Multispectrum fits for the R6 manifold



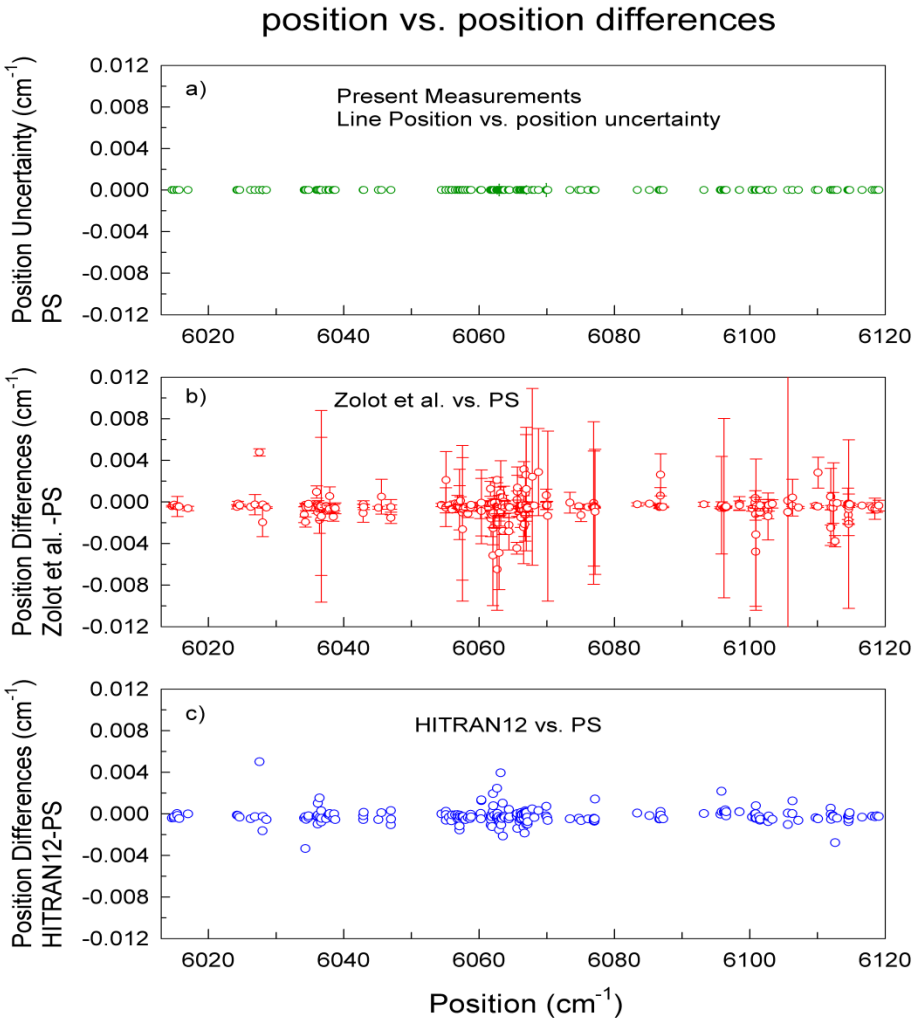


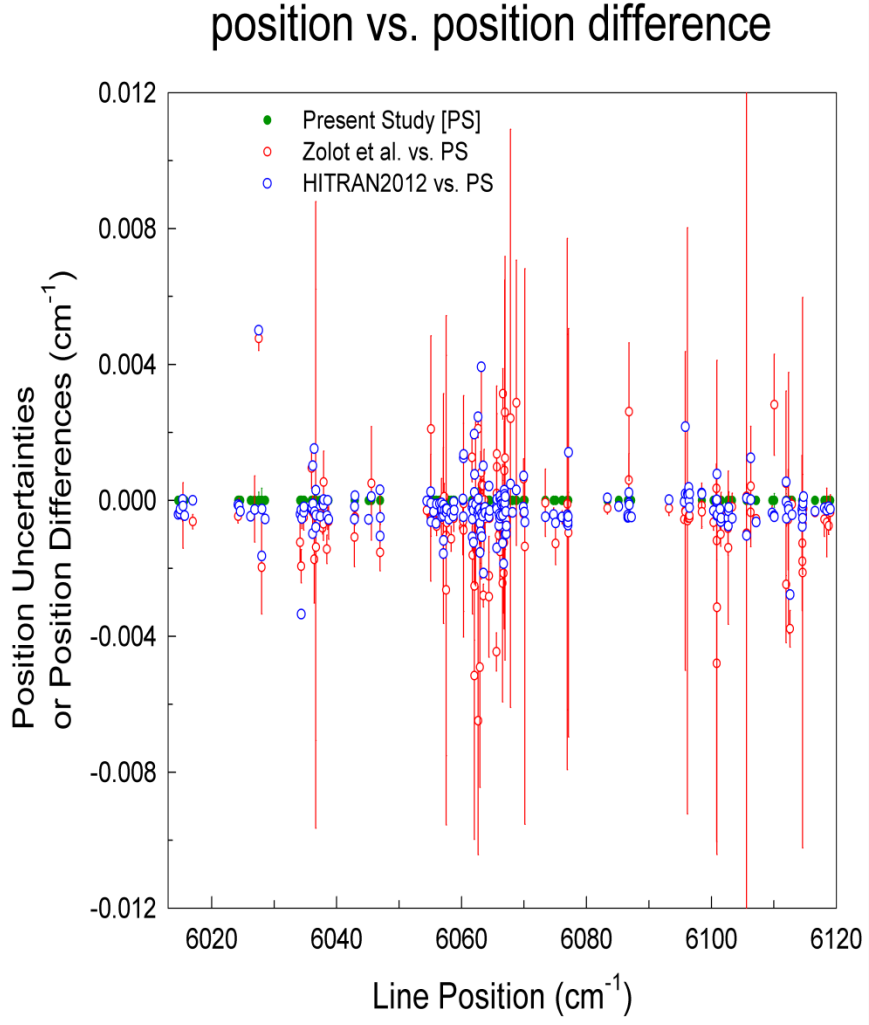
Multispectrum Fittings of the $2\nu_3$ R5 Manifold





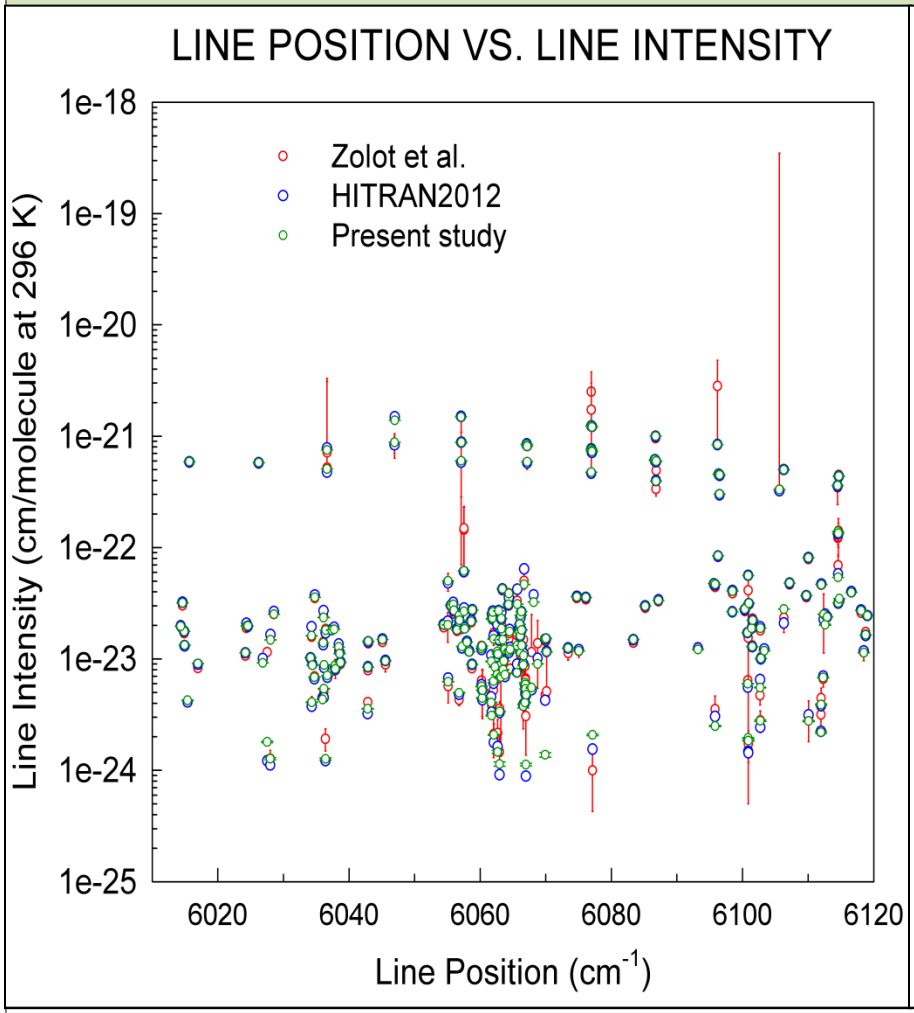
Comparison of Line Positions relative to Zolot et al. and HITRAN2012 Database

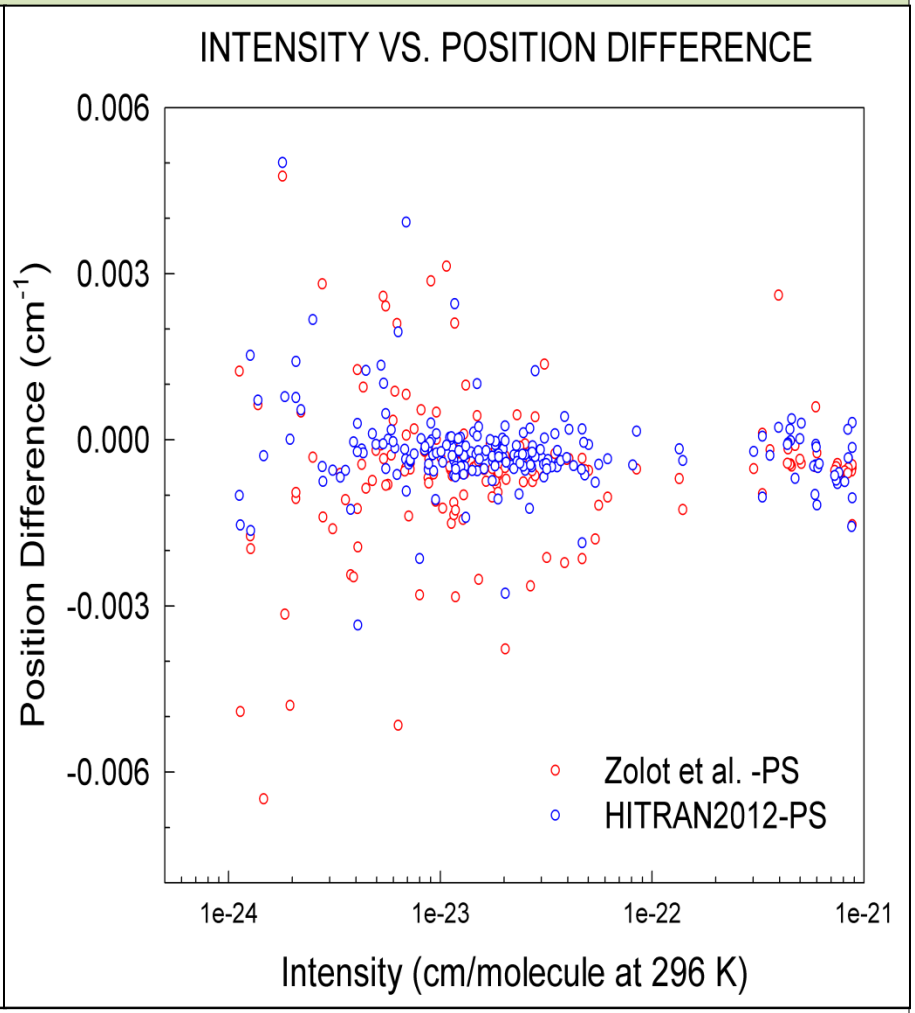




The figures plotted on the left and on the right panels represent the positional differences between present study [PS] vs. Zolot et al. and PS vs. HITRAN2012 database in 2 different formats. The measurement uncertainties in Zolot et. al. are 10 to 30 times worse compared to present measurements.

Comparison of Line Intensities: Present study, Zolot et al. and HITRAN2012 Database





Similar to line position comparison, the line intensities also show large scatter in Zolot et al. measurements compared to [PS].

Comparison of positions and intensities for select transitions in the $2\nu_3$ CH_4

Source	Line	Identification	Position (cm^{-1})	Intensity (cm/molecule at 296 K)
This study [a]	R0	1A2 ← 0A1 1	6015.6638495 (12)	0.58959(5)×10^{-21}
Zolot et al.			6015.66382968 (67)	0.5760 (5)×10^{-21}
HITRAN2012			6015.663830	0.5862×10^{-21}
This study	R1	2F2 ← 1F1 1	6026.2268974 (15)	0.57862 (5) ×10^{-21}
Zolot et al.			6026.22686058 (100)	0.5670 (6) ×10^{-21}
HITRAN2012			6026.226861	0.5768 ×10^{-21}
This study	R2	3E ← 2E 1	6036.6540617 (77)	0.50701 (8) ×10^{-21}
Zolot et al.			Not available	Not available
HITRAN2012			6036.654800	0.4753 e-21
This study	R2	3F1 ← 2F2 1	6036.6575542 (58)	0.74923 (44) e-21
Zolot et al.			Not available	Not available
HITRAN2012			6036.657200	0.7808 ×10^{-21}
This study	R3	4F2 ← 3F1 1	6046.9421498 (31)	0.88037 (6) ×10^{-21}
Zolot et al.			6046.94208818 (7372)	0.856(153) ×10^{-21}
HITRAN2012			6046.942900	0.8325 ×10^{-21}
This study	R3	4F1← 3F2 1	6046.9528285 (190)	0.87949 (7) ×10^{-21} c
Zolot et al.			6046.95171484 (5370)	0.845 (210) ×10^{-21}
HITRAN2012			6046.95220	0.8325 ×10^{-21}
This study	R3	4A1← 3A2 1	6046.9636366 (34)	0.1384 (9) ×10^{-20}
Zolot et al.			6046.96357638 (2035)	0.1410 (60) ×10^{-20}
HITRAN2012			6046.963576	0.1486 ×10^{-20}
This study	R4	5A2 ← 4A1 1	6057.0795581 (28) c	0.14837 (12) ×10^{-20} c
Zolot et al.			6057.07954801 (2635)	0.1490 (80) ×10^{-20}
HITRAN2012			6057.079548	0.1501×10^{-20}
This study	R4	5F2 ← 4F1 1	6057.091933 (23)	0.8744 (10) ×10^{-21} c
Zolot et al.			6057.09180316 (21215)	0.873 (588) ×10^{-21}
HITRAN2012			6057.090800	0.8797 ×10^{-21}
This study	R4	5E ← 4E1 1	6057.1003388 (80) c	0.6003 (12) ×10^{-21} c
Zolot et al.			6057.10053920 (33823)	0.579 (509) ×10^{-21}
HITRAN2012			6057.099600	0.5835 ×10^{-21}
This study	R4	5F1← 4F2 1	6057.126580 (23) c	0.87970 (7) ×10^{-21} c
Zolot et al.			6057.12658722 (133)	0.8720 (12) ×10^{-21}
HITRAN2012			6057.126900	0.8839 ×10^{-21}

[a] Absolute calibration of positions performed relative to Ishibahi et al. [Optics Communications 161 (1999) 223-226].

Comparison of line mixing (ORME): [PS] vs. Tran et al. [a]

Mixing pair (s)	Assignments	ν (cm^{-1})	Self	Air	N_2[a]	T-dependence Self and air	T-dep. N_2[a]
R3 F	4F2 ← 3F1 1 4F1 ← 3F2 1	6046.94259 6046.95327	0.002 (F)	0.004 (F)	0.00346	0.8 (F), 0.8 (F)	0.863
R4 F	5F2 ← 4F1 1 5F1 ← 4F2 1	6057.09237 6057.12702	0.01215 (11)	0.00909 (8)	0.00293	0.807 (5); 0.834 (16)	0.697
R5 F	6F2 ← 5F1 1 6F1 ← 5F2 1	6067.08133 6067.09943	0.00049(6)	0.00282 (3)	0.00063	0.9 (F), 0.9(F)	0.774
R5 F	6F1 ← 5F2 1 6F2 ← 5F1 2	6067.08133 6067.15656	0.01201 (10)	0.00915 (5)	0.01178	0.9 (F), 0.9 (F)	0.782
R6 A	7A1 ← 6A2 1 7A2 ← 6A1 1	6076.95354 6077.06348	0.01939 (8)	0.01810 (4)	0.01548	0.944 (8), 1.015 (6)	0.788
R6 F	7F2 ← 6F1 1 7F1 ← 6F2 2	6077.04705 6077.02853	0.0065 F	0.00728 F	0.00966	0.75 F, 0.75 F	0.747
R6 F	7F2 ← 6F1 1 7F1 ← 6F2 1	6077.04705 6076.93470	0.00065 F	0.0005 F	0.00365	0.75 F, 0.75 F	0.747
R6 F	7F1 ← 6F2 2 7F1 ← 6F2 1	6077.02853 6076.93470	0.00001 F	0.0 F	0.00054	0.75 F	1.011
R7 F	8F1 ← 7F2 2 8F2 ← 7F1 2	6086.77938 6086.83023	0.01351 (11)	0.00355(11)	0.01292	0.7 F, 0.7 F	0.731
R7 F	8F1 ← 7F2 1 8F2 ← 7F1 2	6086.63467 6086.83023	0.01262 (8)	0.01562 (18)	0.00697	0.7 F, 0.7 F	0.731
R7 F	8F2 ← 7F1 1 8F1 ← 7F2 2	6086.62286\ 6086.77938	0.000001 F	0.00015 F	0.00125	0.7 F, 0.7 F	0.709
R8 E	9E ← 8E1 9E ← 8E2	6096.18020 6096.48511	0.01695 (11)	0.01241 (10)	0.00848	0.8 F, 0.8 F	0.814
R8 F	9F2 ← 8F1 2 9F1 ← 8F2 2	6096.42382 6096.50081	0.01996 (4)	0.01410 (4)	0.01815	0.75 F, 0.75 F	0.768

[a] Calculated off-diagonal relaxation matrix element coefficients and their T-dependences from Tran et al. [J Quant Spectrosc Radiat Transfer 111 (2010) 1344-1356] for N_2-broadening

Measured line parameters for select $2\nu_3$ transitions from this study

Line	Self Width[a]	*n* (self W)	Air Width[a]	*n'* (air W)	δ^0 Self shift[a] ($\times10^{-1}$)	δ' Self shift[b] ($\times10^{-4}$)	δ^0 Air shift[a] ($\times10^{-1}$)	δ' Air shift[b] ($\times10^{-4}$)	Speed dep.
R0 A1 1[d]	0.08166 (2) 0.0809 (1)[e]	0.8055 (4) 0.86 (7)[e]	0.06076 91)	0.8051 (5)	-0.1542 (3) -0.174 (1)[e]	0.739 (2) 0.65 (12)[e,f]	-0.1191 (1)	0.420 92)	0.0576 (7)
R1 F1 1[d]	0.08307 (2)	0.8262 (4)	0.06562 (20	0.8578 (5)	-0.1458 (2)	0.719 (2)	-0.1049 (1)	0.164 (3)	0.0556 (7)
R2 E 1	0.07520 (19)	0.8252 (0)	0.05795 (11)	0.8583 (5)	-0.1414 (3)	0.719 (2)	-0.1015 (1)	0.153 (3)	0.0677 (8)
R2 F2 1	0.08480 (12)	0.8252 (0)c	0.06894 (9) c	0.8583 (5)c	-0.1414 (3)	0.720 (3)	-0.1015 (1)	0.153 (3)	0.0677 (8)c
R3 F1 1	0.07987 (4)	0.8199 (0)	0.06762 (1)	0.8224 (8)	-0.1493 (5)	0.749 (6)	-0.0871 (2)	0.312 (4)	0.0601 (9)c
R3 F2 1	0.07987 (4) c	0.8199 (0)c	0.06762 (1) c	0.8224 (8)c	-0.1493 (5) c	0.749 (6)c	-0.0871 (2)c	0.312 (4)c	0.0601 (9)c
R3 A2 1	0.07928 (7)	0.8155 (6)	0.06026 (3)	0.8288 (16)	-0.1373 (18)	0.799 (11)	-0.1315 (4)	0.035 (5)	0.0601 (8)
R4 A1 1	0.07906 (7)	0.8211 (1)	0.06237 (4)	0.8342 (14)	-0.1704 (6)	0.698 (9)	-0.1055 (0)	0.334 (5)	0.0856 (7)c
R4 F1 1	0.08431 (4) c	0.8292 (1)c	0.06603 (5) c	0.7901 (19)c	-0.1041 (5)	0.903 (8)	-0.1040 (2)	0.079 (5)	0.0856 (7)c
R4 E 1	0.08203 (31)	0.8211 (1)c	0.06263 (18) c	0.8342 (14)c	-0.1704 (6)c	0.698 (9)	-0.1055 (0)	0.334 (5)	0.0856 (7)c
R4 F2 1	0.08431 (4)	0.8292 (1)	0.06603 (5)	0.7901 (19)	-0.1041 (5)	0.903 (8)	-0.1040 (2)	0.079 (5)	0.0856 (7)

[a] in cm^{-1} atm^{-1} at 286 K. [b] in cm^{-1} atm^{-1} K^{-1}.
The letter "c" at the end of a parameter denotes that value is constrained to another parameter's value within the same least squares solution.
[d] Dicke narrowing was measured to be 0.0120 (4) and 0.0059 (4) cm^{-1} atm^{-1} at 296 K, respectively, for the R0 and R1 lines.
[d,e] Lyulin et al. J Quant Spectrosc Radiat Transfer 112 (2011) 531-539. Used an exponential expression for δ'.

SUMMARY, CONCLUSION, FUTURE PLANS, ACKNOWLEDGMENTS

1. Between the R0 and R10 manifolds, measurements were obtained for over 530 line positions and intensities, 370 self-broadened halfwidth coefficients, 220 T-dependence exponents of self-broadened width coefficients, 290 self-induced pressure shift coefficients and 230 temperature dependences of self shift coefficients. For air-broadening all of the above parameters have been measured for over 200, 170, 175 and 155 transitions, respectively. Future efforts include similar measurements continued in the Q and R branch manifolds.
2. Speed dependence, line mixing (ORME) and line narrowing parameters for R0 and R1 transitions are experimentally determined.
3. Use of auxiliary parameters were critical in determining the spectral line parameters, especially when multiple transitions are assigned to a single absorption feature; such as in R3 and R6 manifolds.
4. Absolute calibration of line positions will be pursued, if needed, (Present measurements vs. both Zolot et al. & Ishibashi et al.). Presently it has been done relative to Ishibashi's absolute frequency measurement of the saturation absorption line of R0.
5. The present measurements are available to anyone interested in applying the results to atmospheric retrievals.

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