(1) KIT, IMK-ASF-BOD, Karlsruhe, Germany
(2) DLR, IMF, Oberpfaffenhofen, Germany
(3) Univ. Bremen, IUP, Bremen, Germany

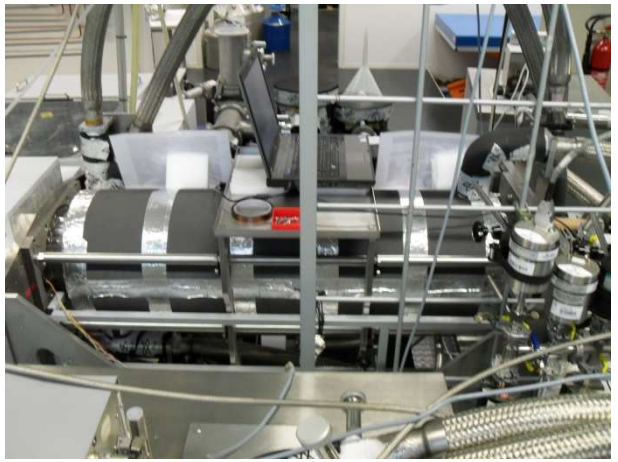
A new CH4 Line List for NDACC-FTIR

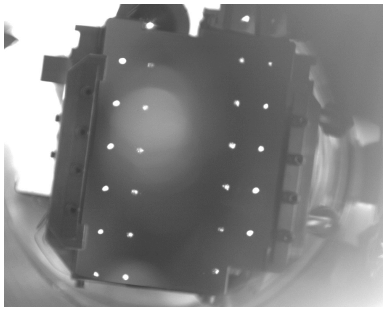
D. Dubravica[(1)], M. Birk[(2)], F. Hase[(1)], J. Loos[(2)], M. Palm[(3)], A. Sadeghi[(3)], G. Wagner[(2)]

KIT, IMK-ASF, Karlsruhe, Germany

Laboratory Measurements

- FTIR measurements at the IMF[2] (DLR[1])
  - Bruker IFS 125HR
  - OPDmax 180 cm, aperture 1 mm
  - Resolution 0.005 cm^{-1}
  - White cell with 80 cm (long path absorption cell)
- 1st measurement series (November 2012)
  - Total absorption lenght 40 m (2x25 reflections)
  - Abscissa calibration with a HBr cell
  - Room temperature (approx. 296 Kelvin)
  - Pure methane with 0.02 / 0.08 / 0.30 / 1.25 / 5.00 mbar
  - Air methane mixture (0.5%) with 30 / 100 / 300 / 1000 mbar
- 2nd measurement series (October 2013)
  - Same adjustments as before
  - Pure methane with 1.0 / 5.0 mbar and 220 / 250 / 330 Kelvin
  - Air methane mixture (0.5%) with 100 / 300 mbar and 220 / 250 / 330 Kelvin
- 3rd measurement series (June 2014)
  - Pure methane with 0.08 / 0.30 / 1.25 / 5.00 mbar (RT, same adjustments as before)





1. DLR, Deutsches Zentrum für Luft- und Raumfahrt / German Aerospace Center, Oberpfaffenhofen, Germany
2. IMF, Institut für Methodik der Fernerkundung / Remote Sensing Technology Institute

HITRAN[1] Database

- HITRAN is an acronym for **hi**gh-resolution **tran**smission molecular absorption database
- The HITRAN database is a compilation of spectroscopic parameters for the simulation of transmission and emission of light in the atmosphere
- The aim of this work is to improve these parameters based on laboratory spectra
- Target parameters are the usual Voigt parameters (line positions, intensities, the air-broadened half-width and the air pressure-induced shift) and additional parameters if required (line shape, line mixing, temperature dependence)

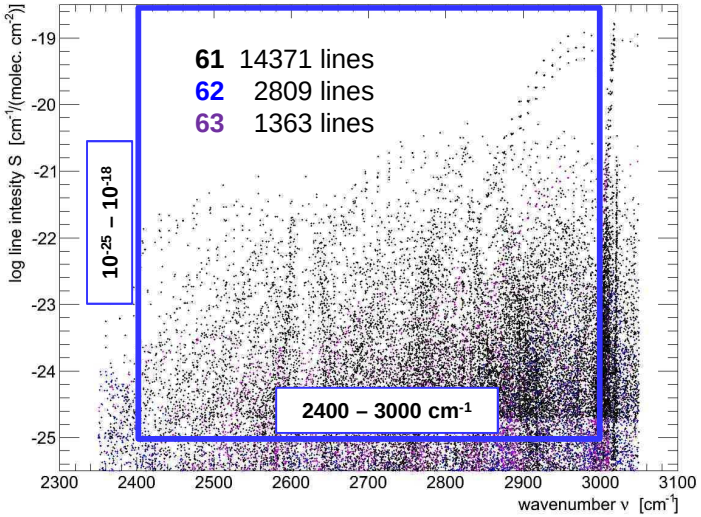
```
61 2593.293767 3.114E-24 1.252E-03.05479.075  376.78570.69-.004755  0 0 0 2 1E   0 0 0 0 1A1   7F1 11     8F2  1   444332453638 7 1 7   45.0  51.0
61 2593.298509 2.271E-23 1.034E-02.06483.071  575.22270.64-.003117  0 0 0 2 1E   0 0 0 0 1A1   10A2  3    10A1  1   344332453638 7 1 7  105.0 105.0
61 2593.306758 6.018E-24 4.649E-03.05494.069  575.25960.64-.006461  0 0 0 2 1E   0 0 0 0 1A1   10F2  9    10F1  2   444332453638 7 1 7   63.0  63.0
```

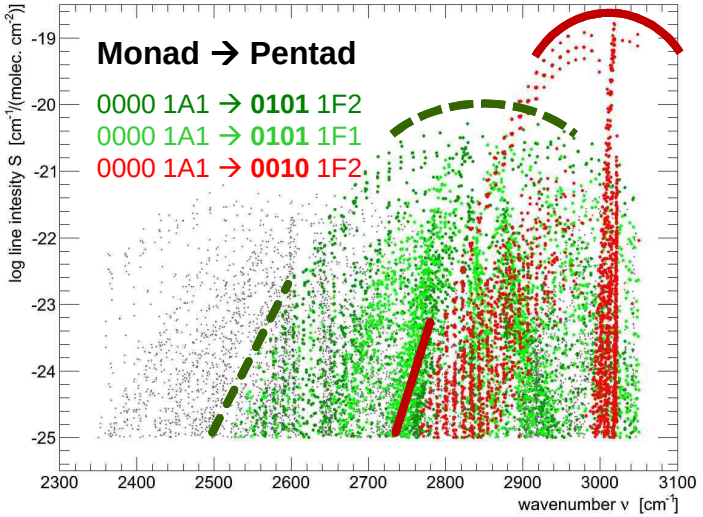
ν_1 (A_1) = 2916 cm^{-1}, ν_2 (E) = 1533 cm^{-1}
ν_3 (F_2) = 3019 cm^{-1}, ν_4 (F_2) = 1311 cm^{-1}

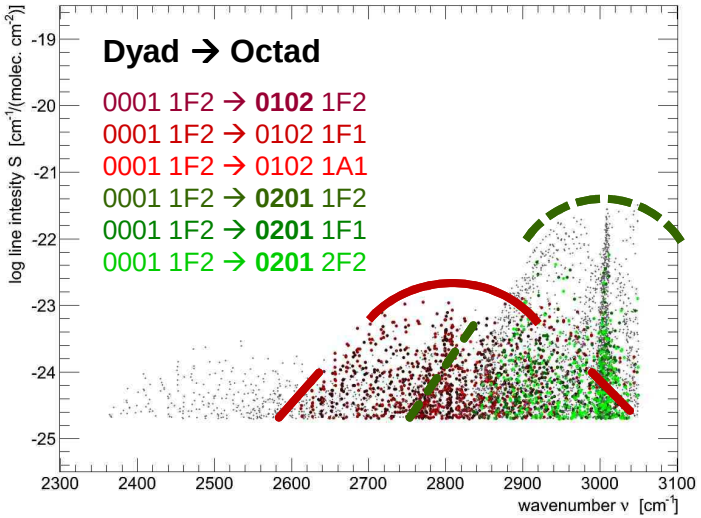
1. HITRAN http://www.cfa.harvard.edu/hitran/

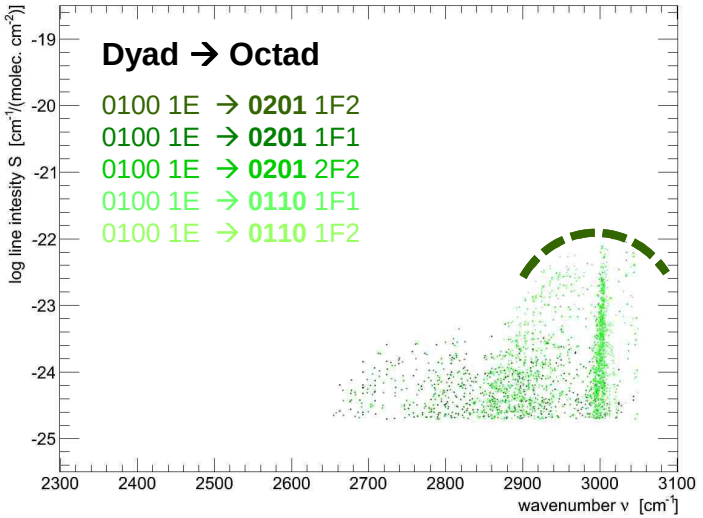
HITRAN 2012

- Total number of lines approx. 18500







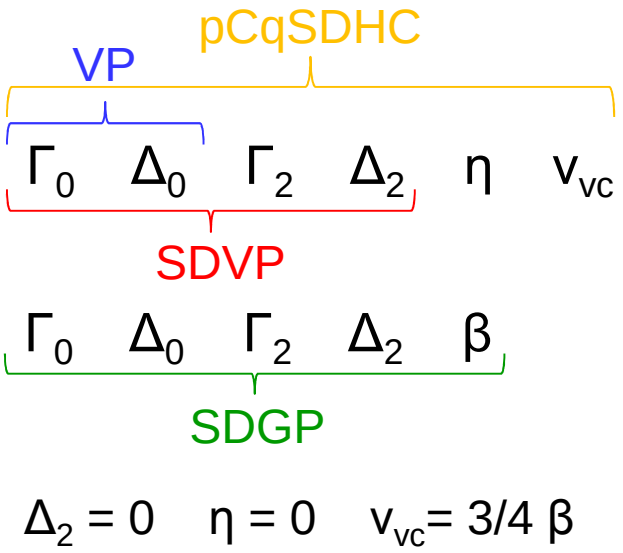


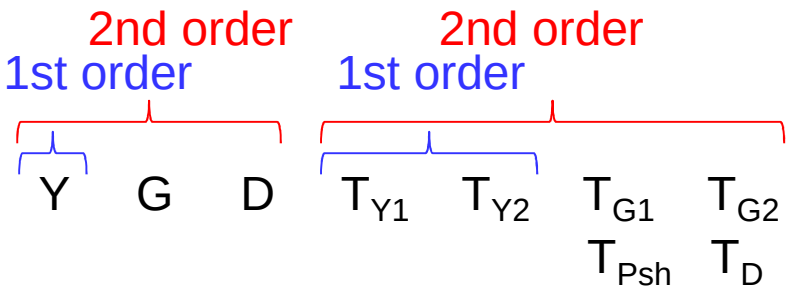
Retrieval Software

- The retrieval software is based on the method of least squares
- The fitting routine performs multi-spectra fits
- It handles line parameters of several lines at a time with additional properly chosen constraints
- Speed Dependent Voigt / Galatry model is implemented for including narrowing effects
- Line Mixing is implemented
- Temperature dependence of the line intensity and shift is included
- Spectral windows were processed iteratively along the spectral range between 2400 and 3000 cm^{-1}

Additional Parameters

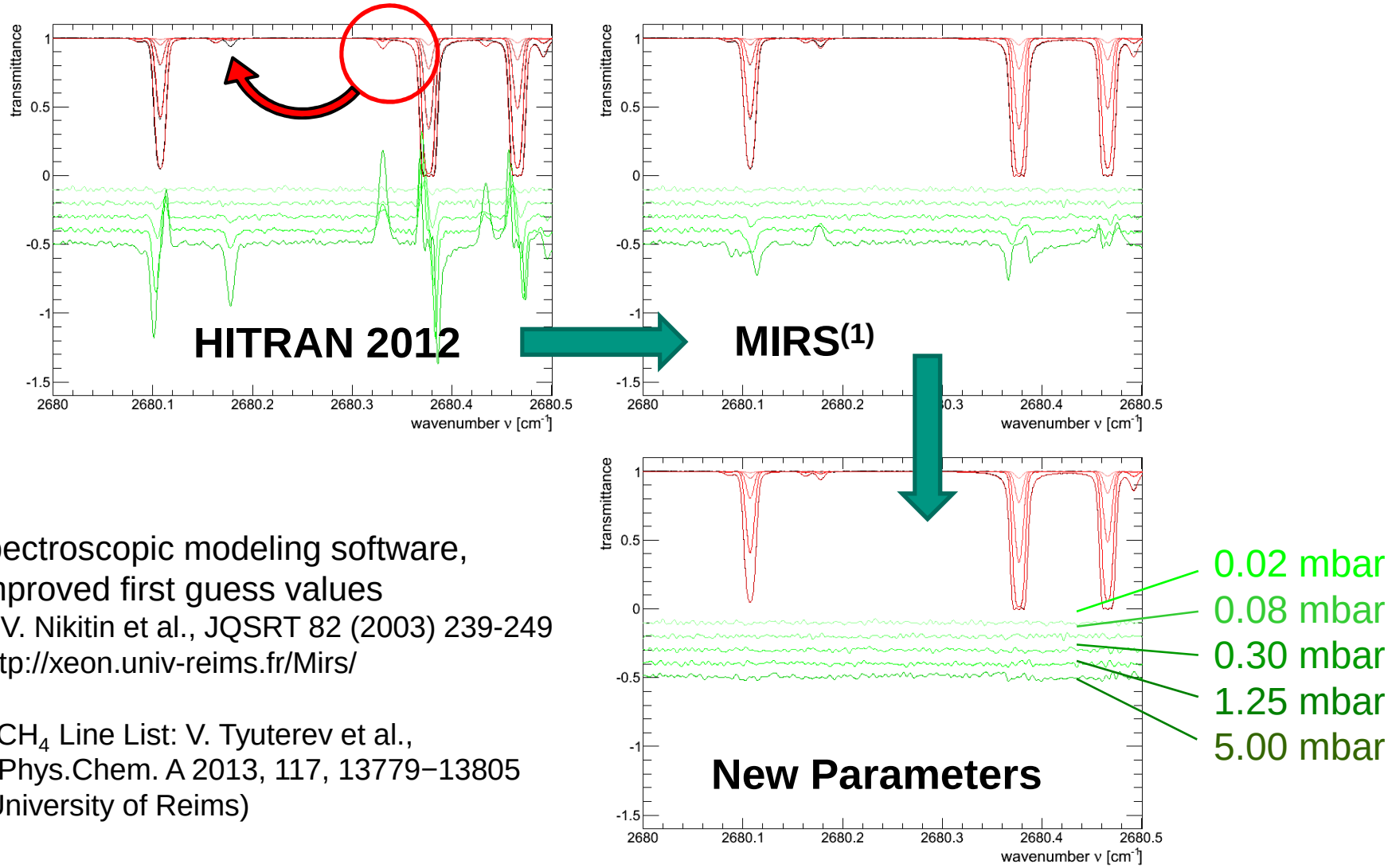
- Speed Dependent Galatry profile
  - pCqSDHC line shape model → Tran[1]
    (partially-Correlated quadratic-Speed-Dependent Hard-Collision model)
  - Some parameters can be set to Zero
- Line Mixing
  - First order approximation → Rosenkranz[2]
  - Second order approximation → Smith[3]
- Temperature Dependence
  - Line Width: $(T_{ref}/T)^{Par}$
  - Line Shift → Smith[4]: (Tref – T) Par
  - Line Intensity E‘‘





[1] H. Tran et al., JQSRT 129, 89-100 (2013)
[2] P. W. Rosenkranz, IEEE Trans Ant. and Prop. AP-23 No 4, 498 (1975)
[3] E. W. Smith, J. Chem. Phys. 74, 6658 (1981)
[4] M. A. H. Smith, SpecChim Acta Vol. 48A No 9, 1257-1272 (1992)

Misplaced and Missing Lines (pure CH_4)

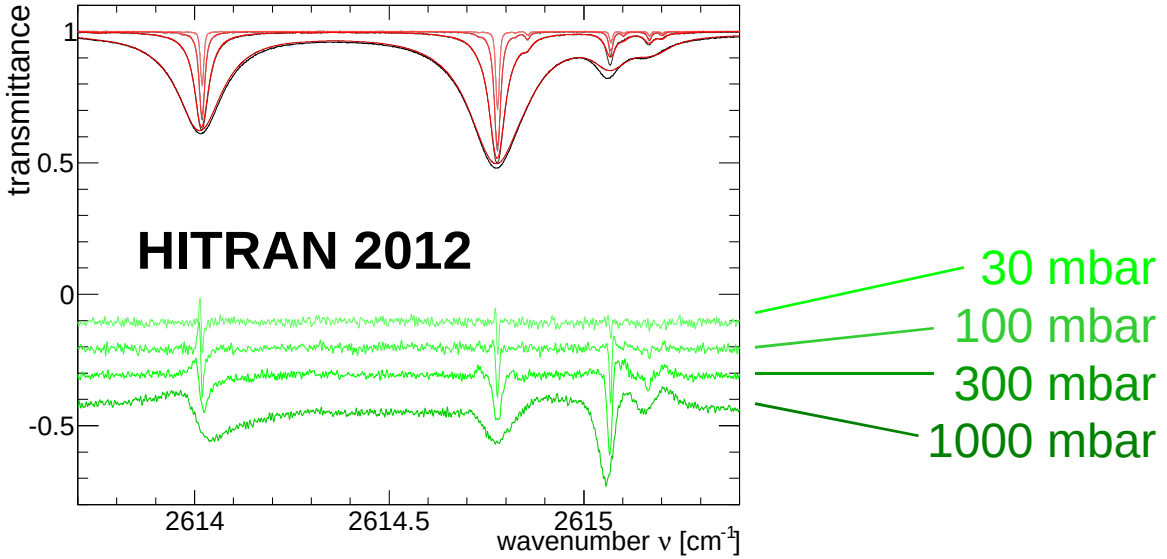


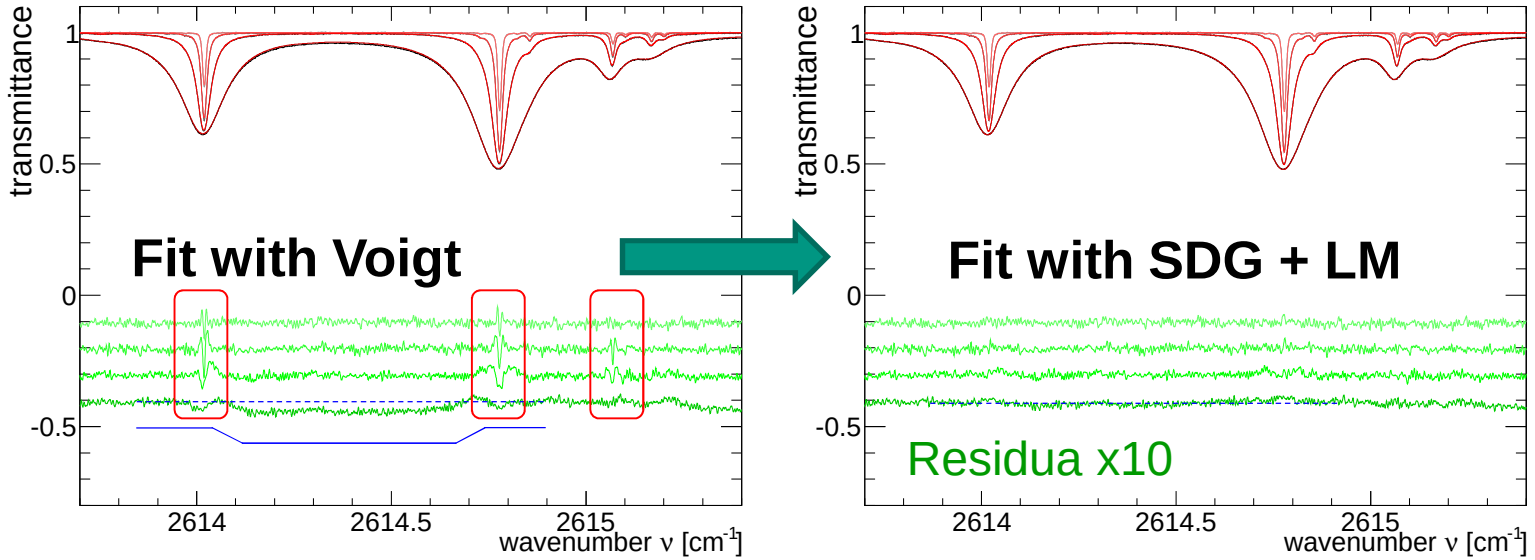
(1) spectroscopic modeling software, improved first guess values
A.V. Nikitin et al., JQSRT 82 (2003) 239-249
http://xeon.univ-reims.fr/Mirs/

$^{12}CH_4$ Line List: V. Tyuterev et al., J.Phys.Chem. A 2013, 117, 13779−13805 (University of Reims)

Voigt → SDG + LM (Air-CH_4 Mixture)

- Mixture (0.5% CH_4)
- NDACC Microwindow 2613.7 – 2615.8 cm^{-1}
- W-Shaped residua
- Line mixing





Overview (Laboratory Spectra)

	MW 1	MW 2	MW 3	MW 4	MW 5	MW 6
CH_4 RT						
Air+CH_4 RT						
CH_4 Temp.						
Air+CH_4 Temp.						

Microwindow is good

Something is wrong
(LM, missing Lines, …)

MW 1: 2611.6 – 2613.3 cm^{-1}
MW 2: 2613.7 – 2615.4 cm^{-1}
MW 3: 2835.5 – 2835.8 cm^{-1}
MW 4: 2903.8 – 2903.9 cm^{-1}
MW 5: 2914.7 – 2915.1 cm^{-1}
MW 6: 2941.5 – 2942.2 cm^{-1}

Self Broadened Spectra (pure CH_4)

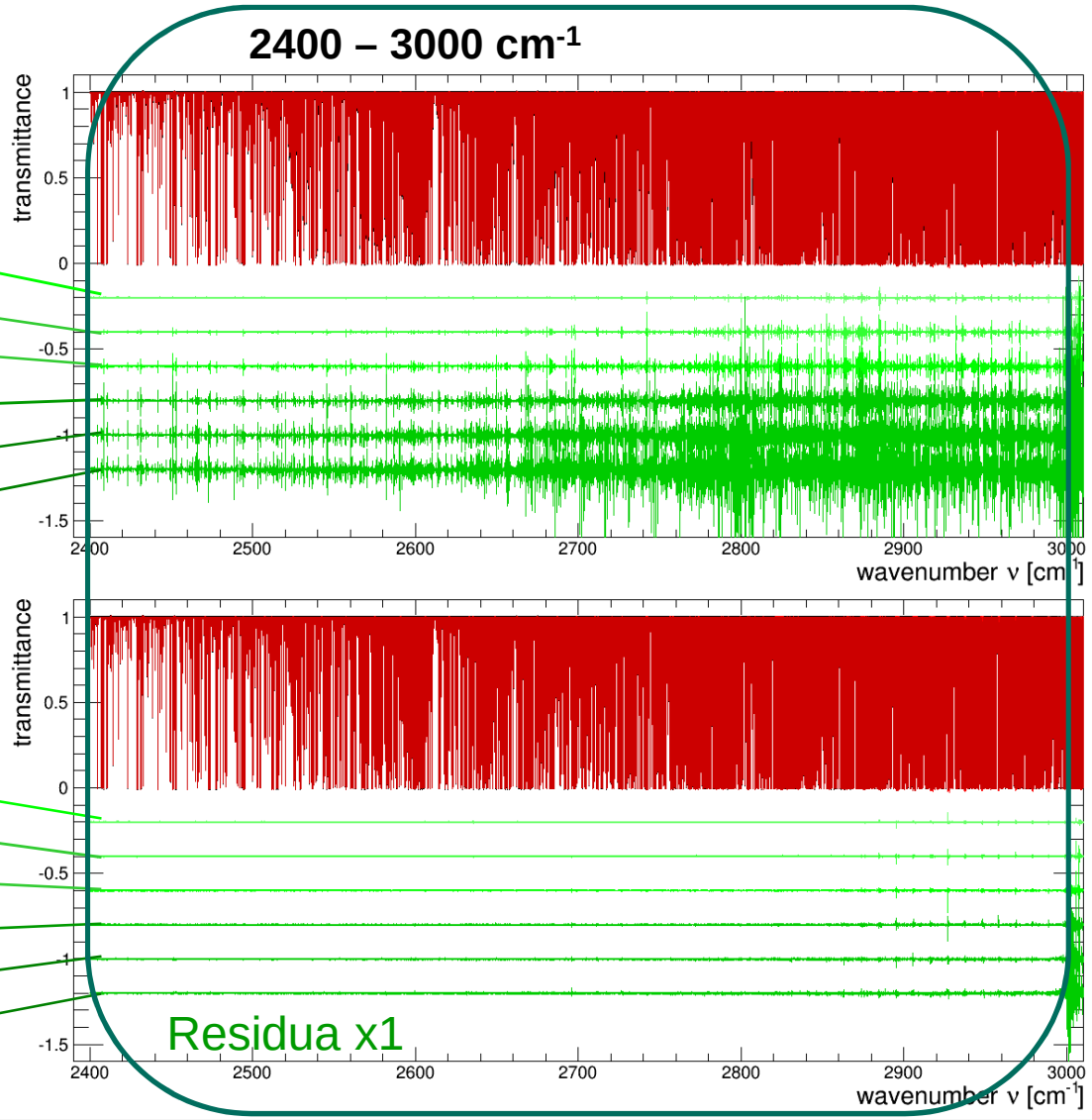
- Room Temperature

HITRAN 2012

0.02 mbar (40m)
0.08 mbar (40m)
0.30 mbar (40m)
1.25 mbar (40m)
5.00 mbar (40m)
5.00 mbar (100m)

New Line List 2015

0.02 mbar (40m)
0.08 mbar (40m)
0.30 mbar (40m)
1.25 mbar (40m)
5.00 mbar (40m)
5.00 mbar (100m)



Self Broadened Spectra (pure CH_4)

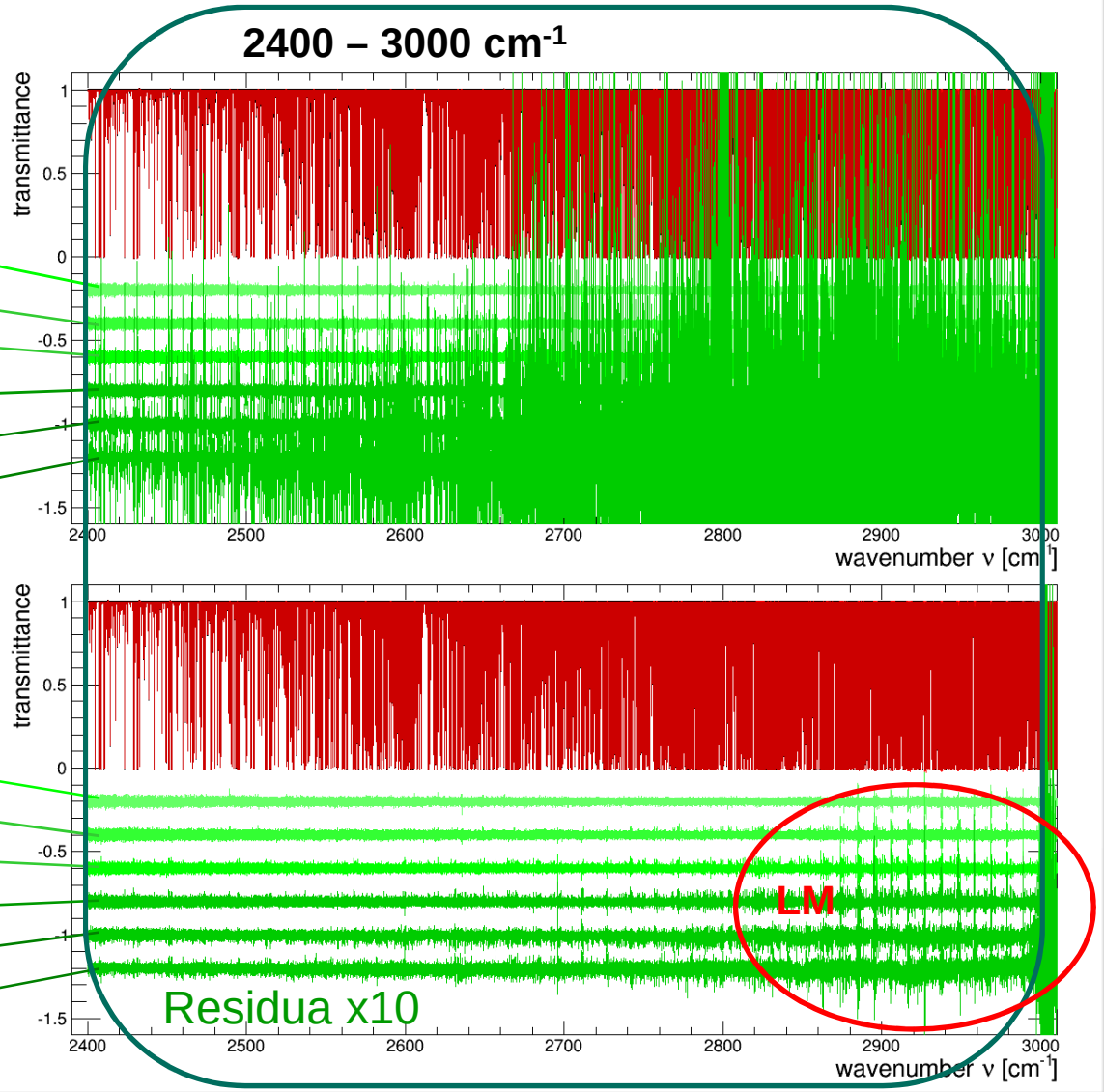
- Room Temperature

HITRAN 2012

0.02 mbar (40m)
0.08 mbar (40m)
0.30 mbar (40m)
1.25 mbar (40m)
5.00 mbar (40m)
5.00 mbar (100m)

New Line List 2015

0.02 mbar (40m)
0.08 mbar (40m)
0.30 mbar (40m)
1.25 mbar (40m)
5.00 mbar (40m)
5.00 mbar (100m)



Overview

	MW 1	MW 2	MW 3	MW 4	MW 5	MW 6
CH_4 RT	✓	✓	✓	✓	✓	✓
Air+CH_4 RT						
CH_4 Temp.						
Air+CH_4 Temp.						

✓ Microwindow is good

? Something is wrong (LM, missing Lines, …)

MW 1: 2611.6 – 2613.3 cm^{-1}
MW 2: 2613.7 – 2615.4 cm^{-1}
MW 3: 2835.5 – 2835.8 cm^{-1}
MW 4: 2903.8 – 2903.9 cm^{-1}
MW 5: 2914.7 – 2915.1 cm^{-1}
MW 6: 2941.5 – 2942.2 cm^{-1}

Air Broadened Spectra (Mixture with 0.5% CH_4)

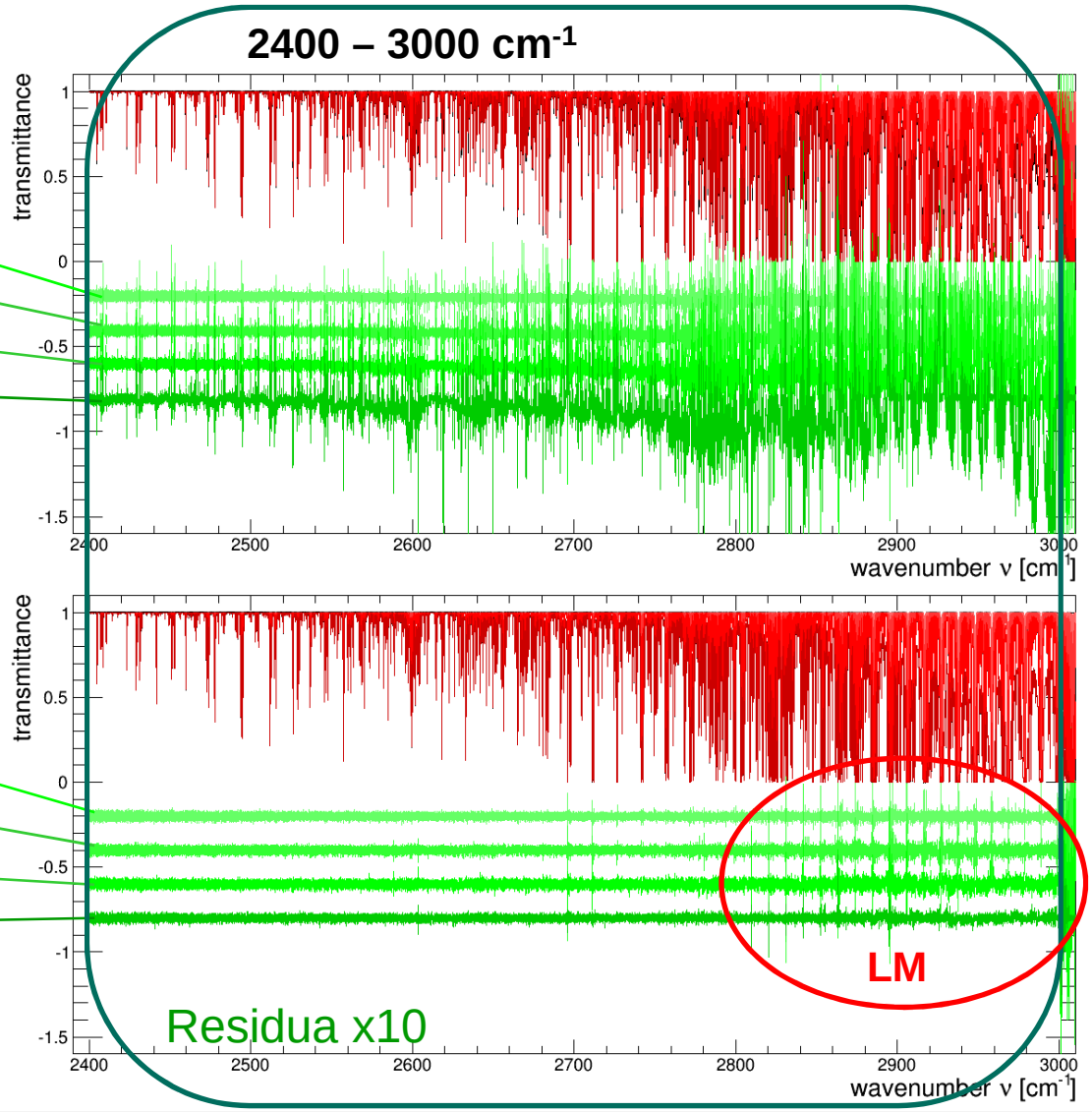
- Room Temperature

HITRAN 2012

30 mbar (296K)
100 mbar (296K)
300 mbar (296K)
1000 mbar (296K)

New Line List 2015

30 mbar (296K)
100 mbar (296K)
300 mbar (296K)
1000 mbar (296K)



NDACC Microwindows (Mix at Room Temperature)

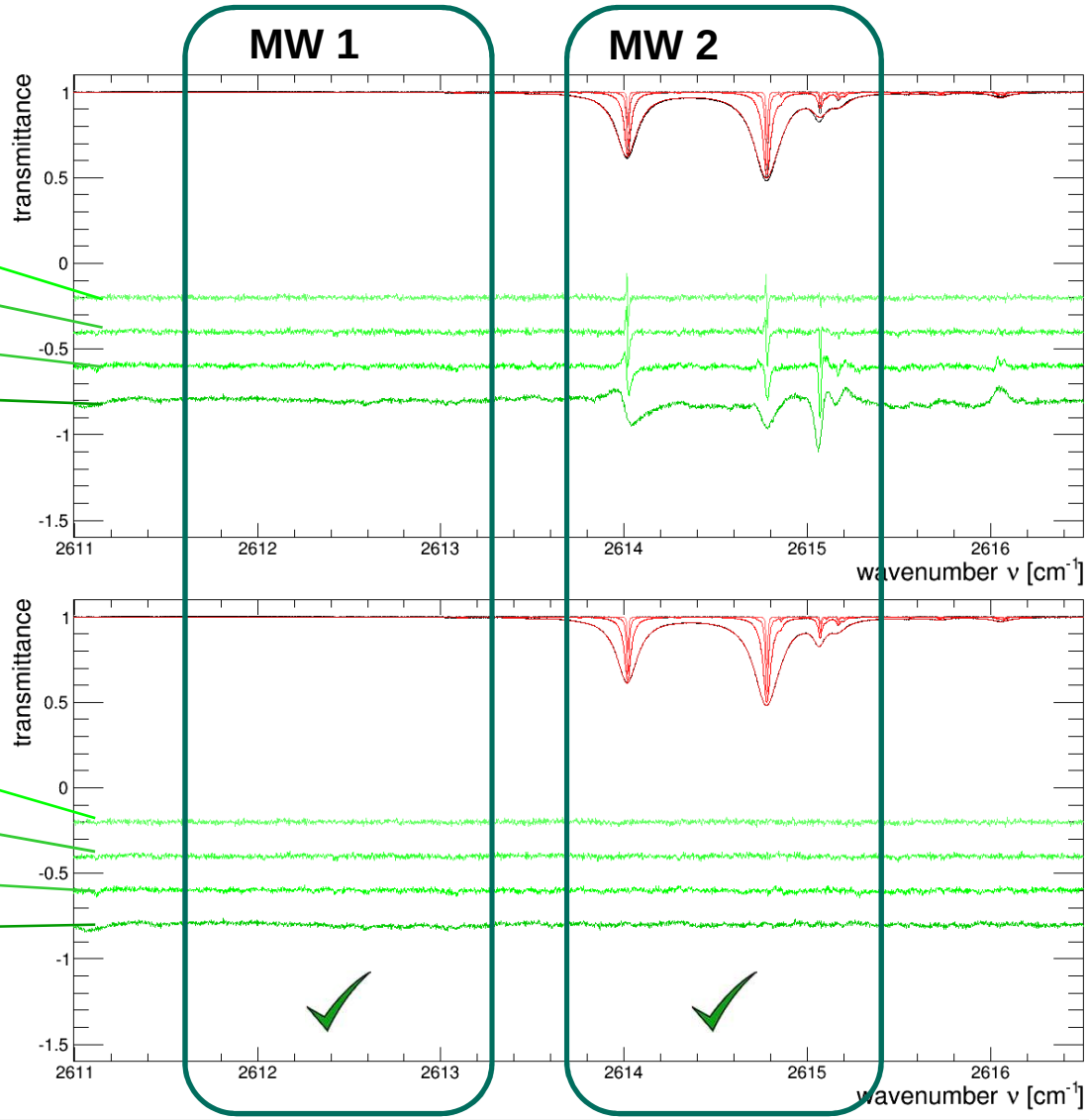
- **MW 1**: 2611.6 – 2613.3 cm^{-1}
- **MW 2**: 2613.7 – 2615.4 cm^{-1}

HITRAN 2012

30 mbar (296K)
100 mbar (296K)
300 mbar (296K)
1000 mbar (296K)

New Line List 2015

30 mbar (296K)
100 mbar (296K)
300 mbar (296K)
1000 mbar (296K)



NDACC Microwindows (Mix at Room Temperature)

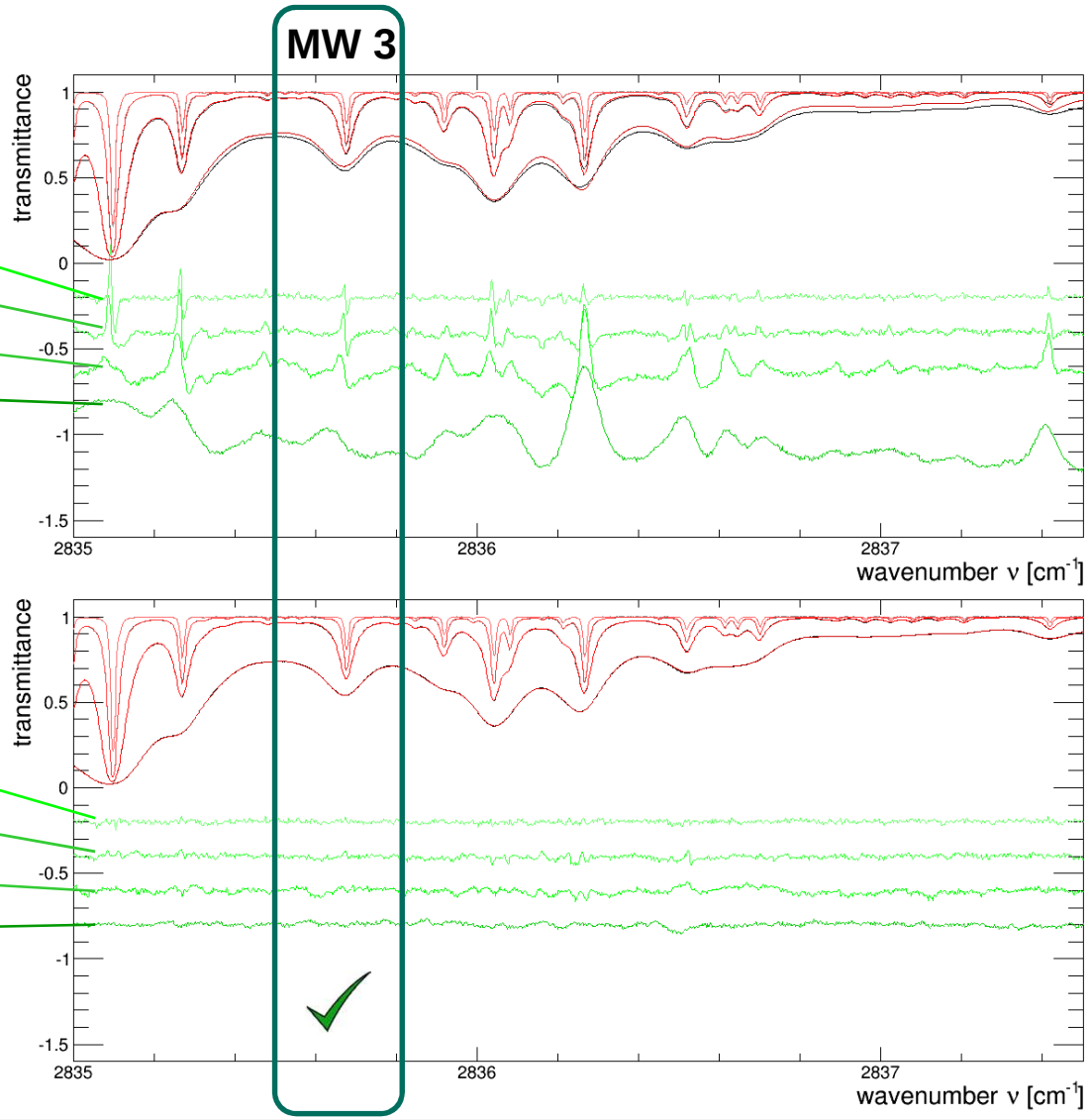
- **MW 3**: 2835.5 – 2835.8 cm^{-1}

HITRAN 2012

30 mbar (296K)
100 mbar (296K)
300 mbar (296K)
1000 mbar (296K)

New Line List 2015

30 mbar (296K)
100 mbar (296K)
300 mbar (296K)
1000 mbar (296K)



NDACC Microwindows (Mix at Room Temperature)

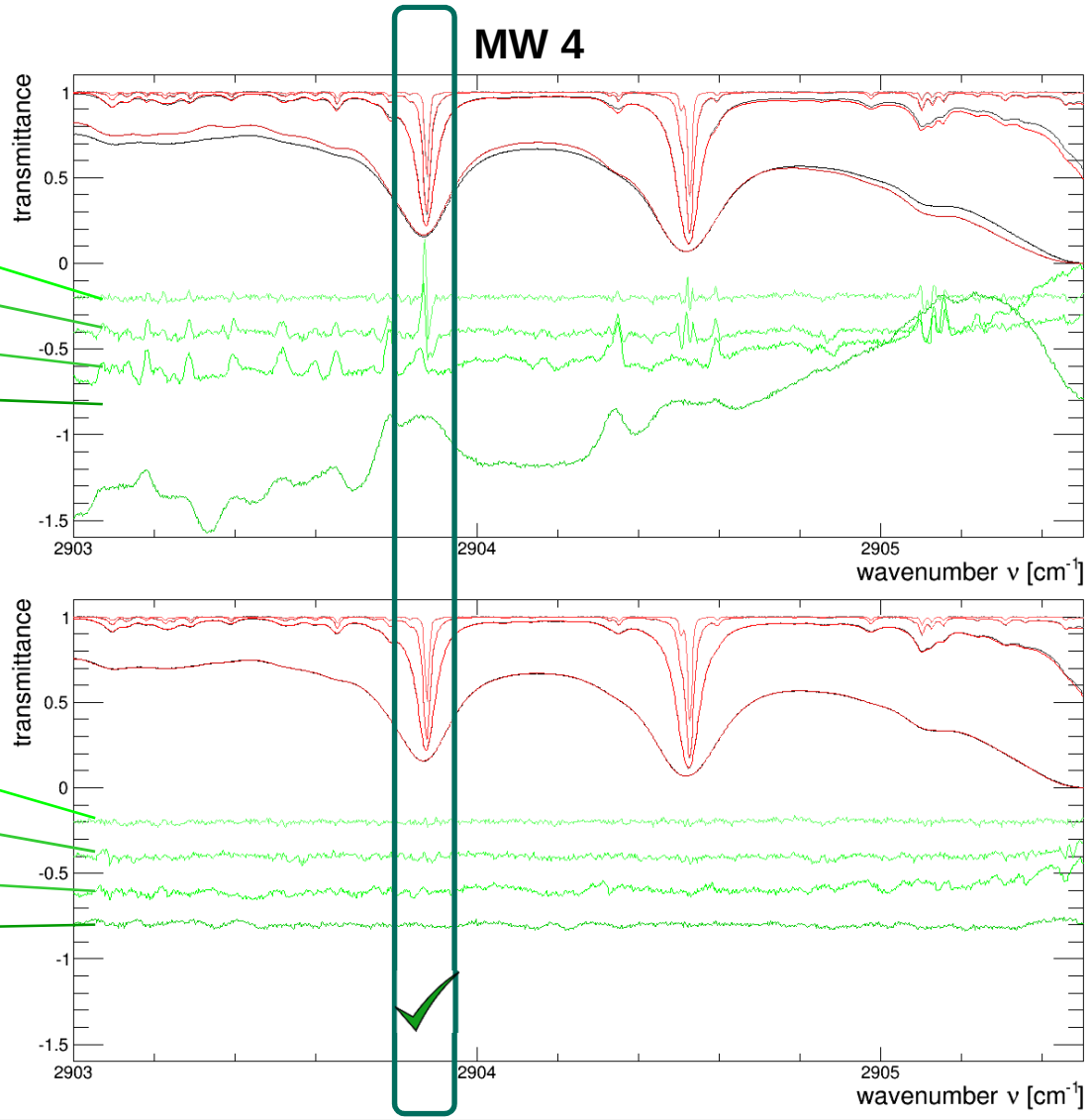
- **MW 4**: 2903.8 – 2903.9 cm^{-1}

HITRAN 2012

30 mbar (296K)
100 mbar (296K)
300 mbar (296K)
1000 mbar (296K)

New Line List 2015

30 mbar (296K)
100 mbar (296K)
300 mbar (296K)
1000 mbar (296K)



NDACC Microwindows (Mix at Room Temperature)

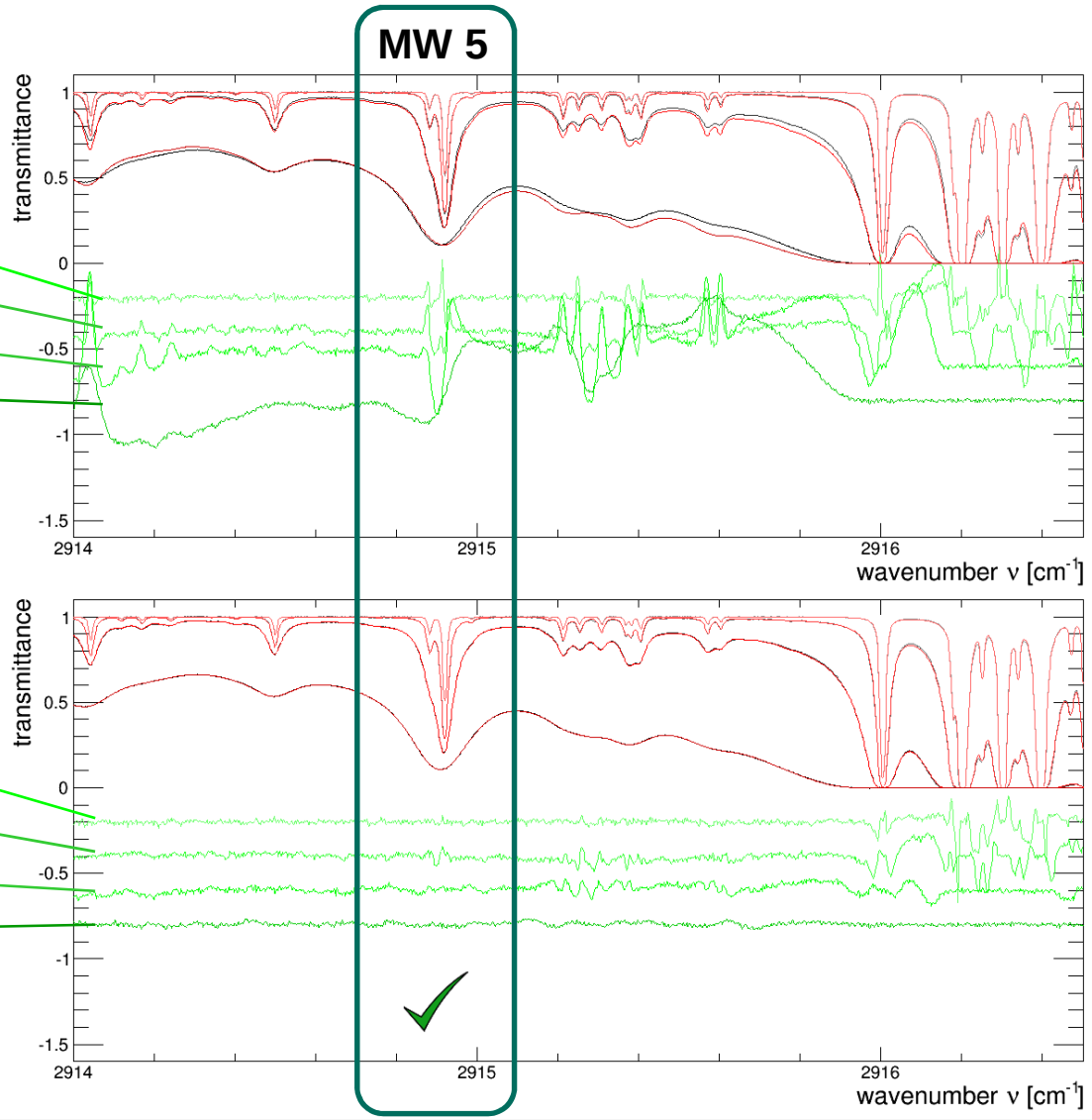
- **MW 5**: 2914.7 – 2915.1 cm^{-1}

HITRAN 2012

30 mbar (296K)
100 mbar (296K)
300 mbar (296K)
1000 mbar (296K)

New Line List 2015

30 mbar (296K)
100 mbar (296K)
300 mbar (296K)
1000 mbar (296K)



NDACC Microwindows (Mix at Room Temperature)

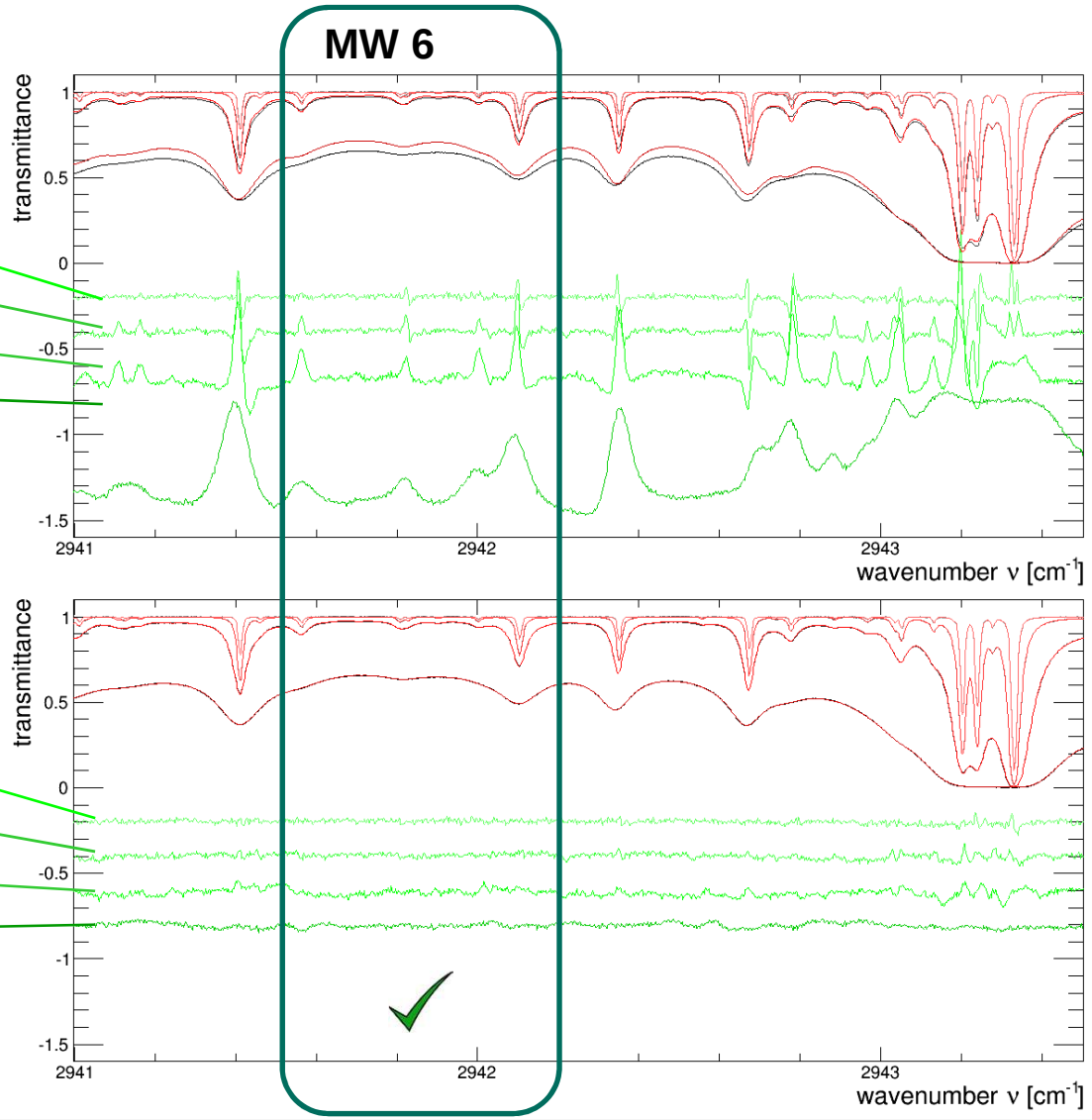
- **MW 6**: 2941.5 – 2942.2 cm^{-1}

HITRAN 2012

30 mbar (296K)
100 mbar (296K)
300 mbar (296K)
1000 mbar (296K)

New Line List 2015

30 mbar (296K)
100 mbar (296K)
300 mbar (296K)
1000 mbar (296K)



Overview

	MW 1	MW 2	MW 3	MW 4	MW 5	MW 6
CH_4 RT	✓	✓	✓	✓	✓	✓
Air+CH_4 RT	✓	✓	✓	✓	✓	✓
CH_4 Temp.						
Air+CH_4 Temp.						

✓ Microwindow is good

? Something is wrong (LM, missing Lines, …?)

MW 1: 2611.6 – 2613.3 cm^{-1}
MW 2: 2613.7 – 2615.4 cm^{-1}
MW 3: 2835.5 – 2835.8 cm^{-1}
MW 4: 2903.8 – 2903.9 cm^{-1}
MW 5: 2914.7 – 2915.1 cm^{-1}
MW 6: 2941.5 – 2942.2 cm^{-1}

Self Broadened Spectra (pure CH_4)

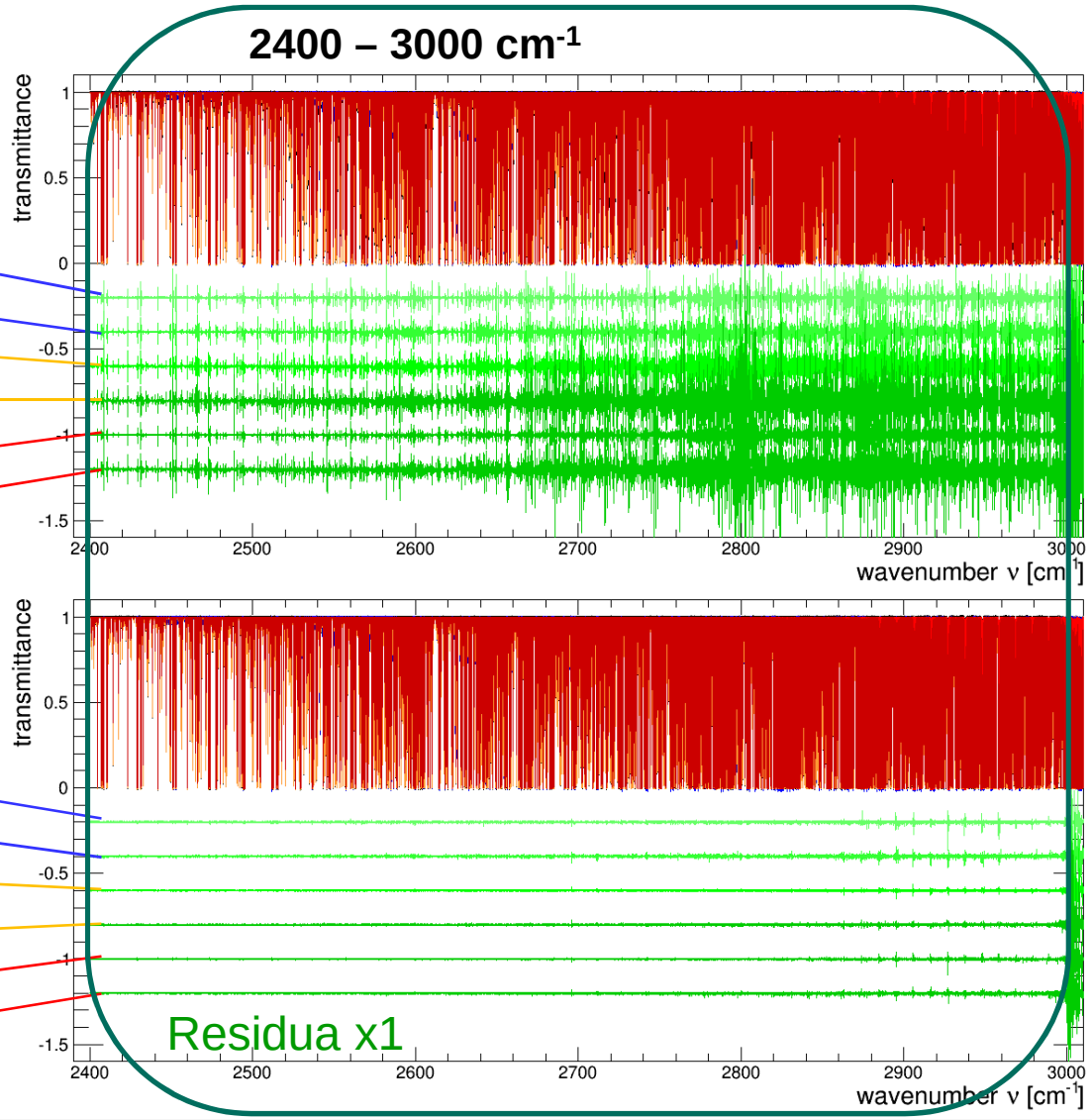
- Temperature dependence

HITRAN 2012

1 mbar (198K,40m)
5 mbar (198K,40m)
5 mbar (296K,40m)
5 mbar (296K,100m)
1 mbar (333K,40m)
5 mbar (333K,40m)

New Line List 2015

1 mbar (198K,40m)
5 mbar (198K,40m)
5 mbar (296K,40m)
5 mbar (296K,100m)
1 mbar (333K,40m)
5 mbar (333K,40m)



Self Broadened Spectra (pure CH_4)

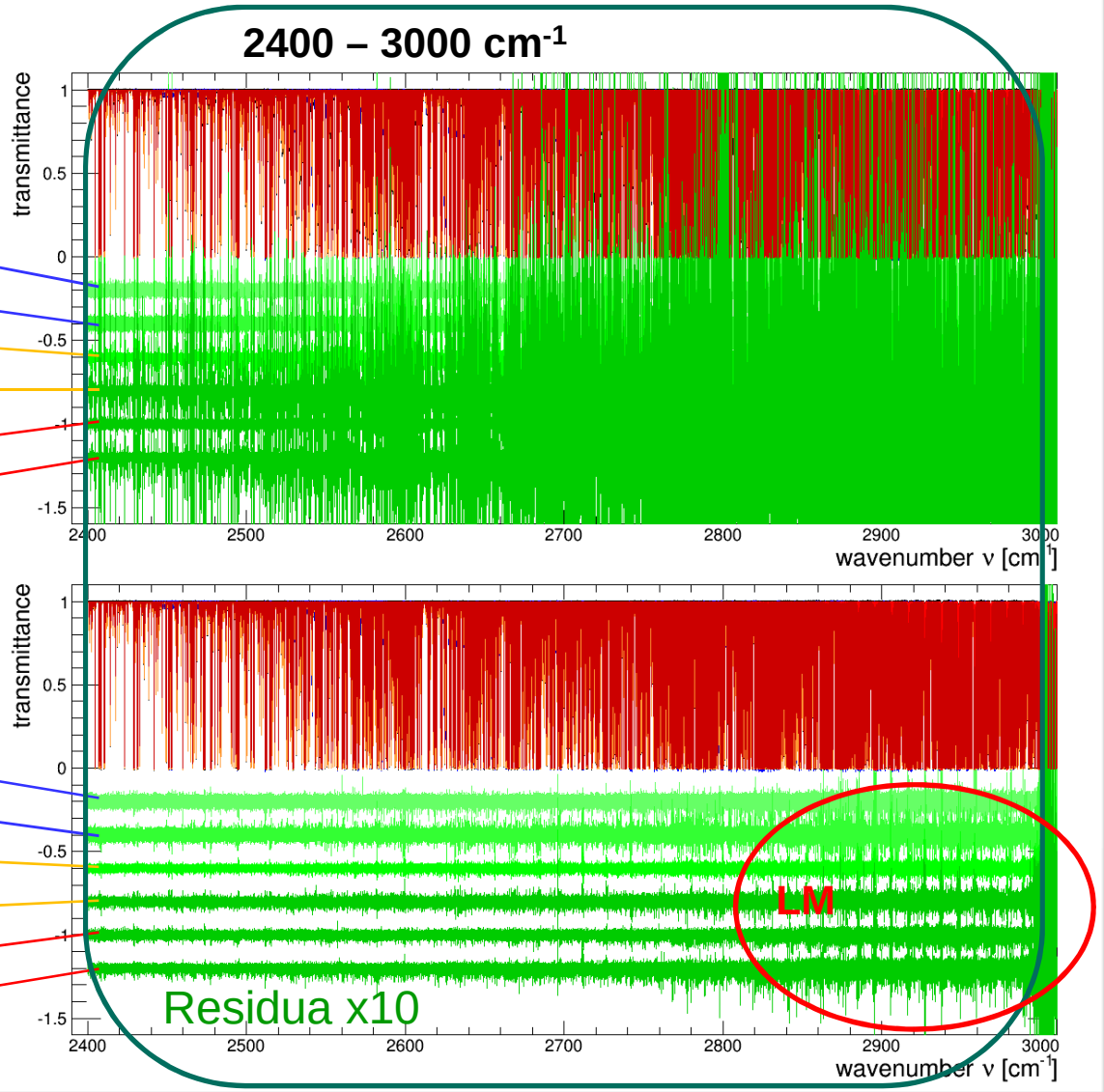
- Temperature dependence

HITRAN 2012

1 mbar (198K,40m)
5 mbar (198K,40m)
5 mbar (296K,40m)
5 mbar (296K,100m)
1 mbar (333K,40m)
5 mbar (333K,40m)

New Line List 2015

1 mbar (198K,40m)
5 mbar (198K,40m)
5 mbar (296K,40m)
5 mbar (296K,100m)
1 mbar (333K,40m)
5 mbar (333K,40m)



Overview

	MW 1	MW 2	MW 3	MW 4	MW 5	MW 6
CH_4 RT	✓	✓	✓	✓	✓	✓
Air+CH_4 RT	✓	✓	✓	✓	✓	✓
CH_4 Temp.	✓	✓	✓	✓	✓	✓
Air+CH_4 Temp.						
30 mbar						
100 mbar						
300 mbar						
1000 mbar						

Air Broadened Spectra (Mixture with 0.5% CH_4)

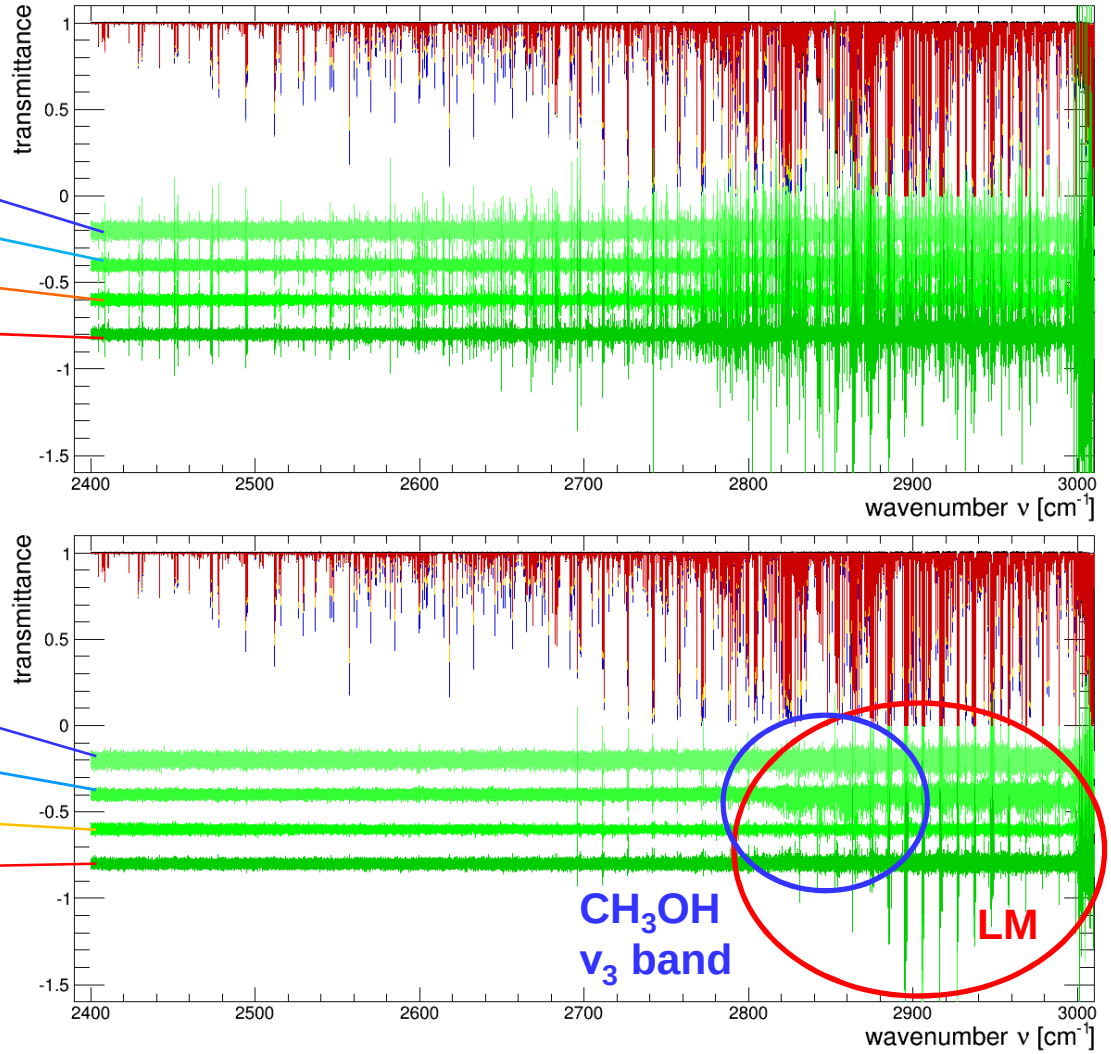
- Temperature dependence

HITRAN 2012

30 mbar (223K)
30 mbar (248K)
30 mbar (296K)
30 mbar (333K)

New Line List 2015

30 mbar (223K)
30 mbar (248K)
30 mbar (296K)
30 mbar (333K)



Overview

	MW 1	MW 2	MW 3	MW 4	MW 5	MW 6
CH_4 RT	✓	✓	✓	✓	✓	✓
Air+CH_4 RT	✓	✓	✓	✓	✓	✓
CH_4 Temp.	✓	✓	✓	✓	✓	✓
Air+CH_4 Temp.						
30 mbar	✓	✓	✓	✓	✓	✓
100 mbar						
300 mbar						
1000 mbar						

Air Broadened Spectra (Mixture with 0.5% CH_4)

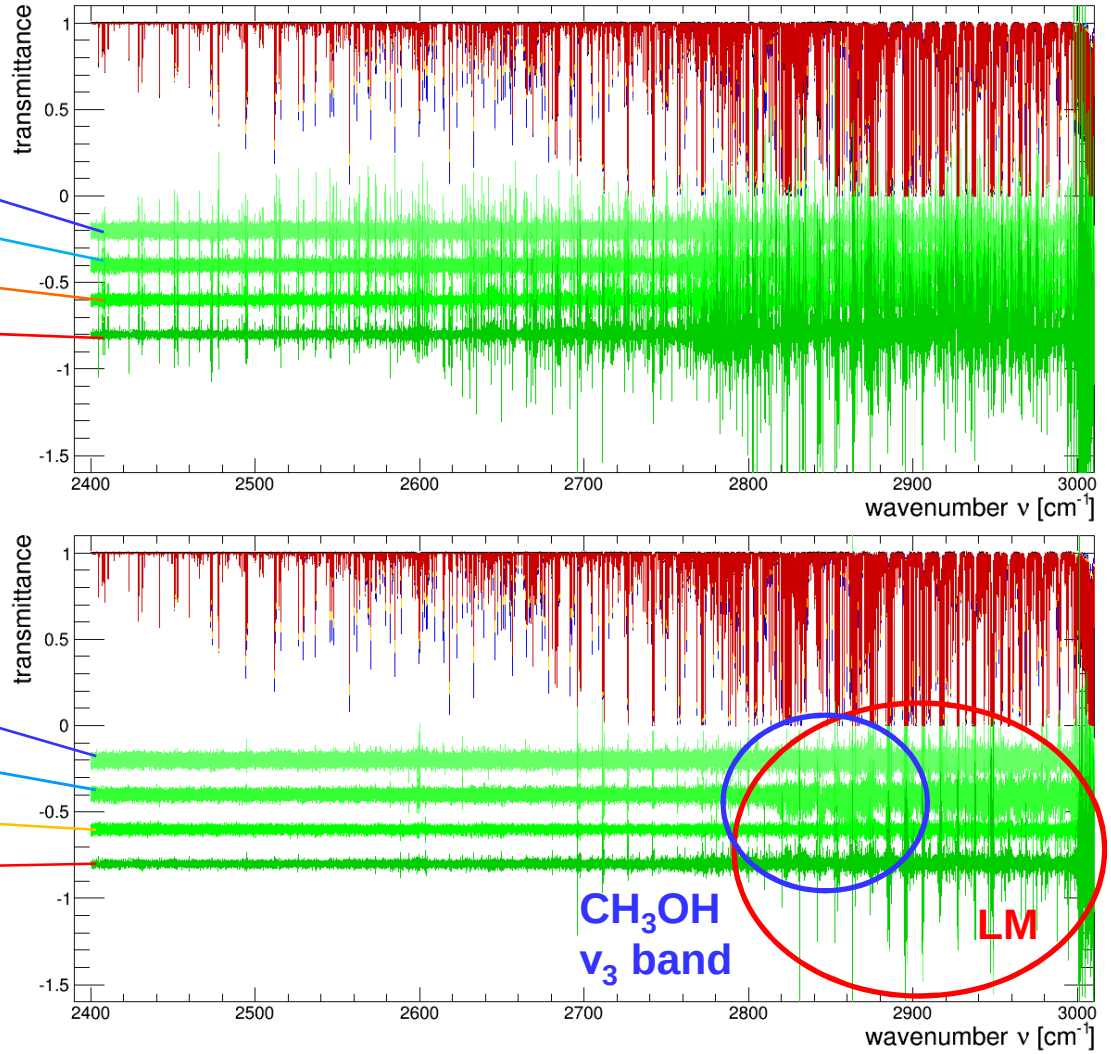
- Temperature dependence

HITRAN 2012

100 mbar (223K)
100 mbar (248K)
100 mbar (296K)
100 mbar (333K)

New Line List 2015

100 mbar (223K)
100 mbar (248K)
100 mbar (296K)
100 mbar (333K)



NDACC Microwindows (Mix, Various Temperatures)

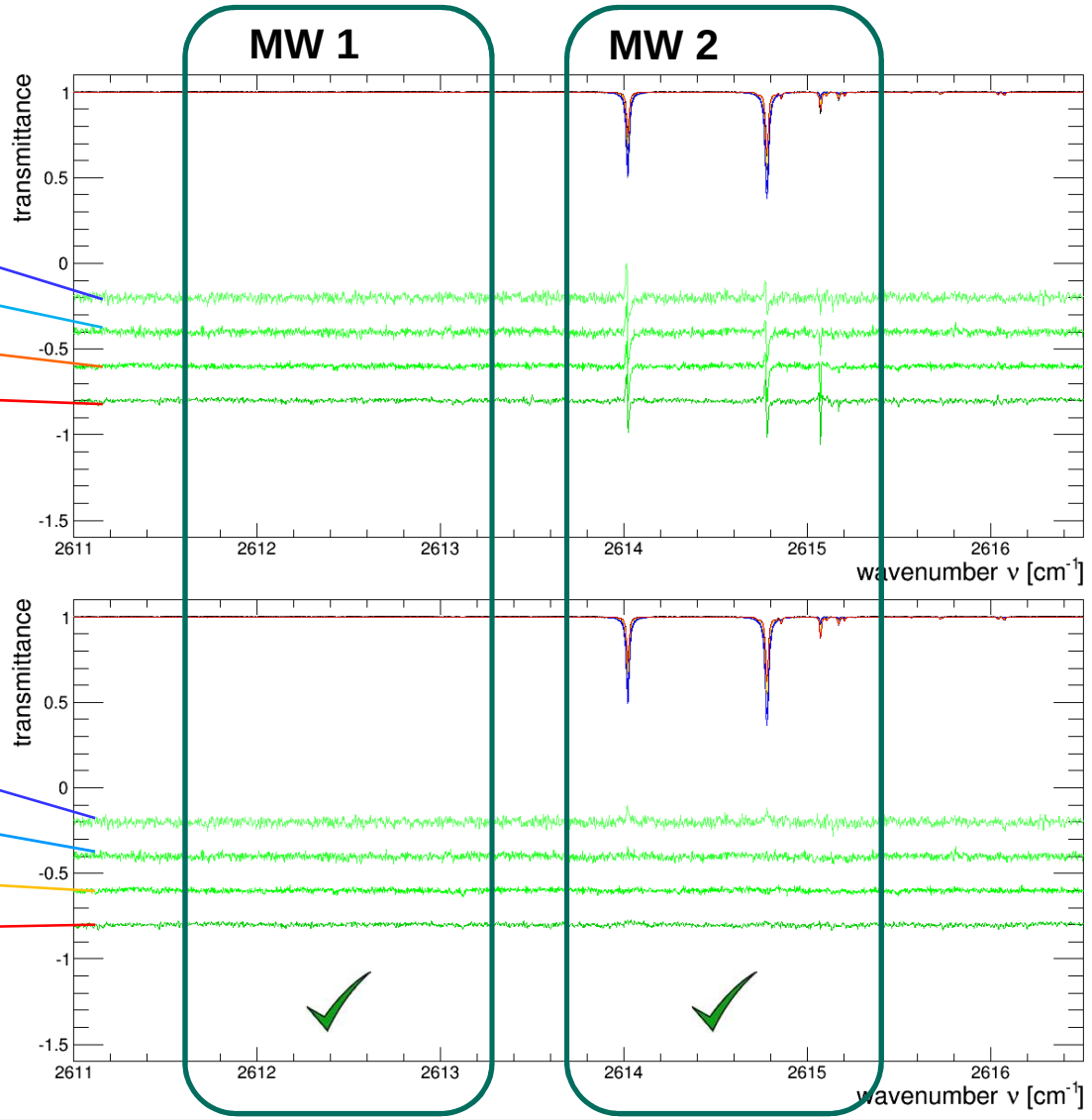
- **MW 1**: 2611.6 – 2613.3 cm^{-1}
- **MW 2**: 2613.7 – 2615.4 cm^{-1}

HITRAN 2012

100 mbar (223K)
100 mbar (248K)
100 mbar (296K)
100 mbar (333K)

New Line List 2015

100 mbar (223K)
100 mbar (248K)
100 mbar (296K)
100 mbar (333K)



NDACC Microwindows (Mix, Various Temperatures)

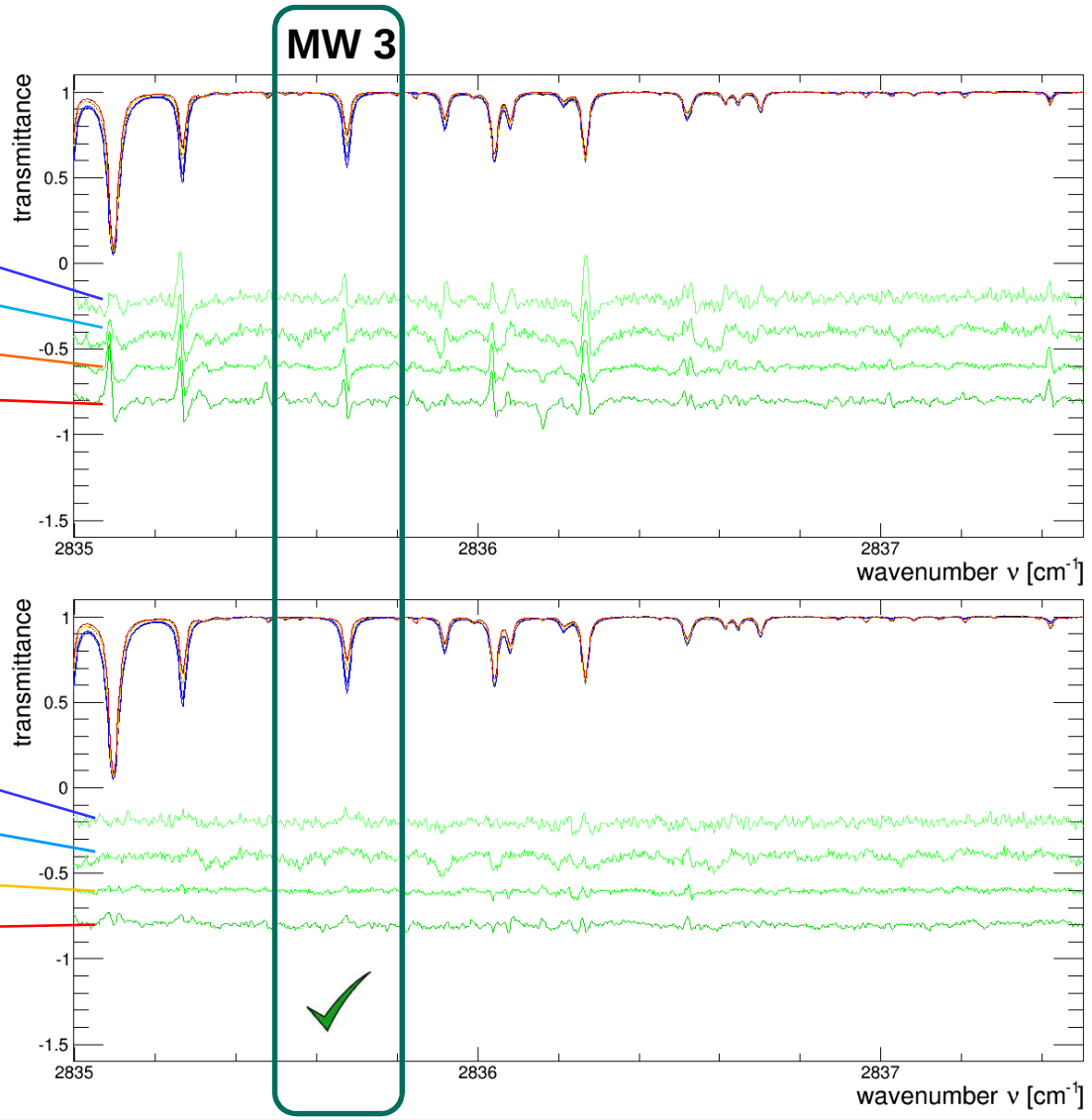
- **MW 3**: 2835.5 – 2835.8 cm^{-1}

HITRAN 2012

100 mbar (223K)
100 mbar (248K)
100 mbar (296K)
100 mbar (333K)

New Line List 2015

100 mbar (223K)
100 mbar (248K)
100 mbar (296K)
100 mbar (333K)



NDACC Microwindows (Mix, Various Temperatures)

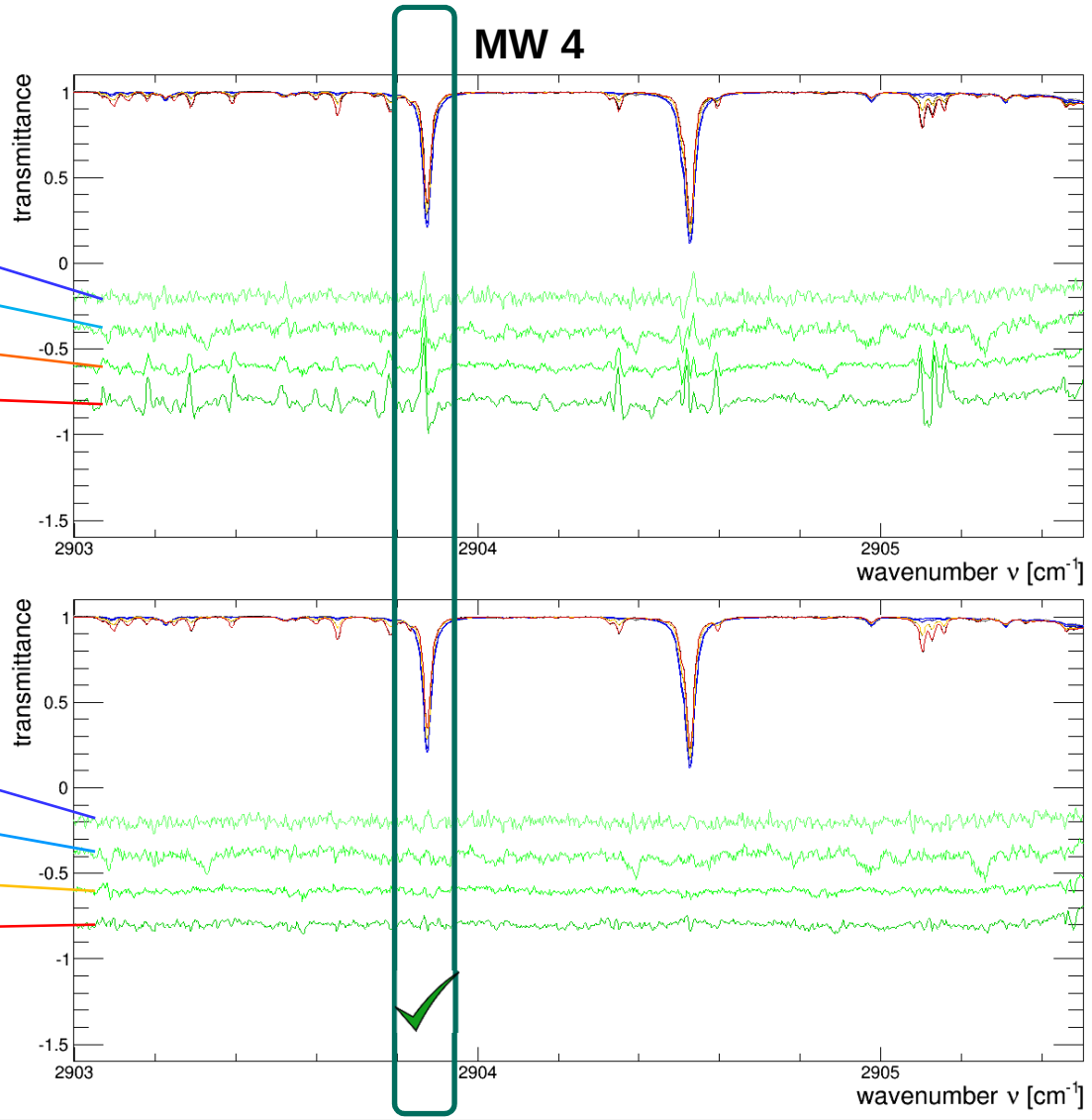
- **MW 4**: 2903.8 – 2903.9 cm^{-1}

HITRAN 2012

100 mbar (223K)
100 mbar (248K)
100 mbar (296K)
100 mbar (333K)

New Line List 2015

100 mbar (223K)
100 mbar (248K)
100 mbar (296K)
100 mbar (333K)



NDACC Microwindows (Mix, Various Temperatures)

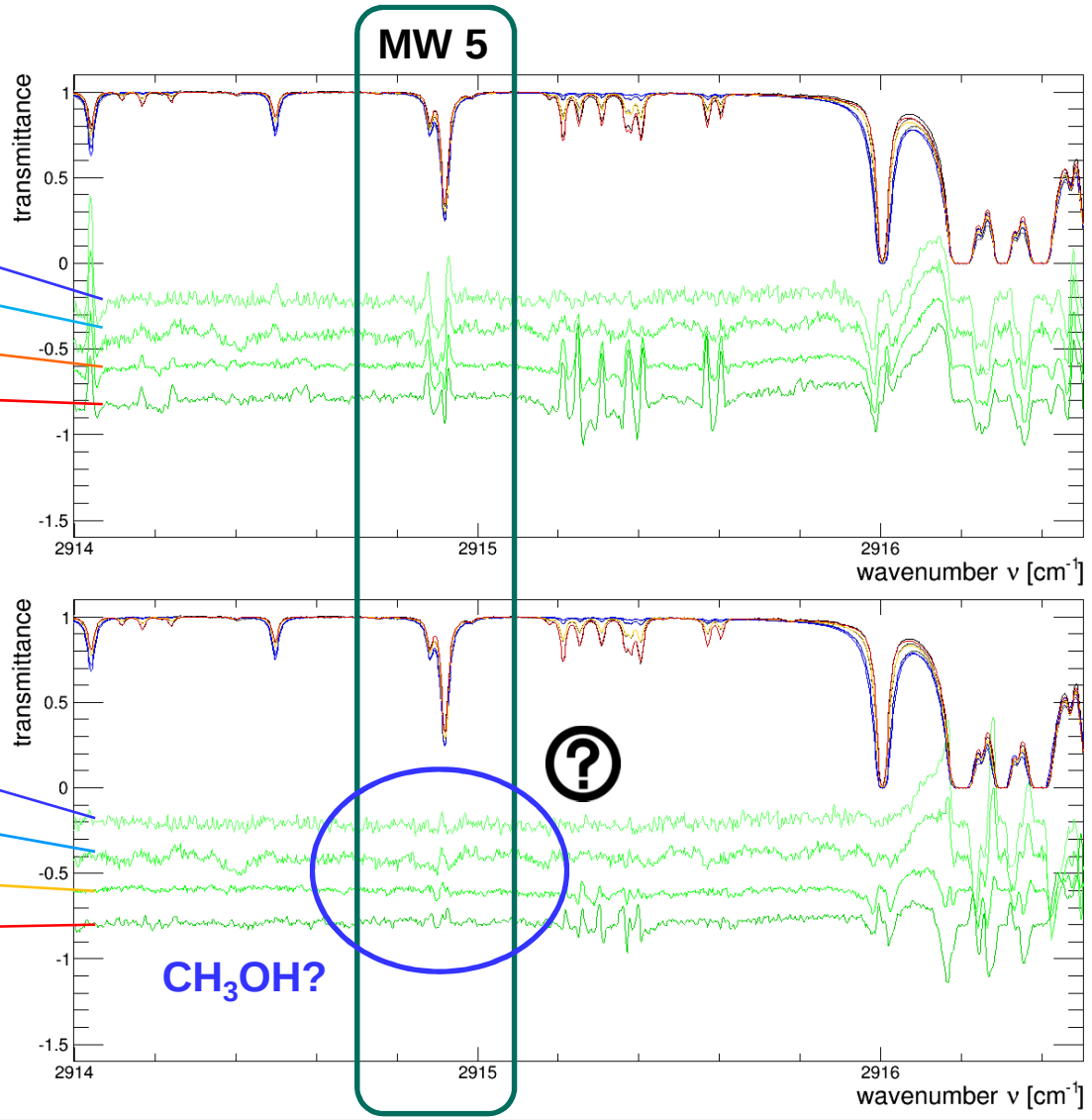
- **MW 5**: 2914.7 – 2915.1 cm^{-1}

HITRAN 2012

100 mbar (223K)
100 mbar (248K)
100 mbar (296K)
100 mbar (333K)

New Line List 2015

100 mbar (223K)
100 mbar (248K)
100 mbar (296K)
100 mbar (333K)



NDACC Microwindows (Mix, Various Temperatures)

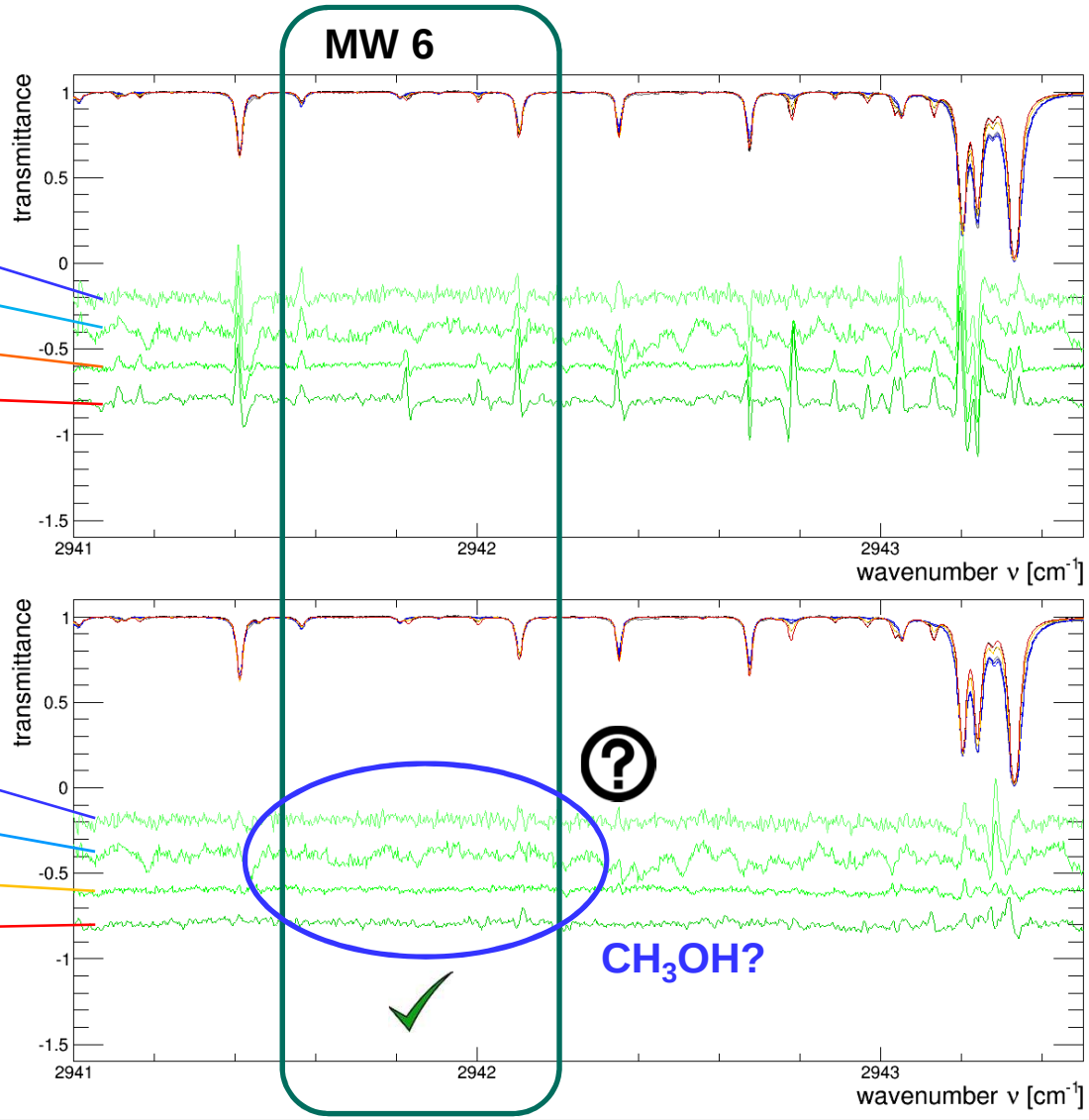
- **MW 6**: 2941.5 – 2942.2 cm^{-1}

HITRAN 2012

100 mbar (223K)
100 mbar (248K)
100 mbar (296K)
100 mbar (333K)

New Line List 2015

100 mbar (223K)
100 mbar (248K)
100 mbar (296K)
100 mbar (333K)



Overview

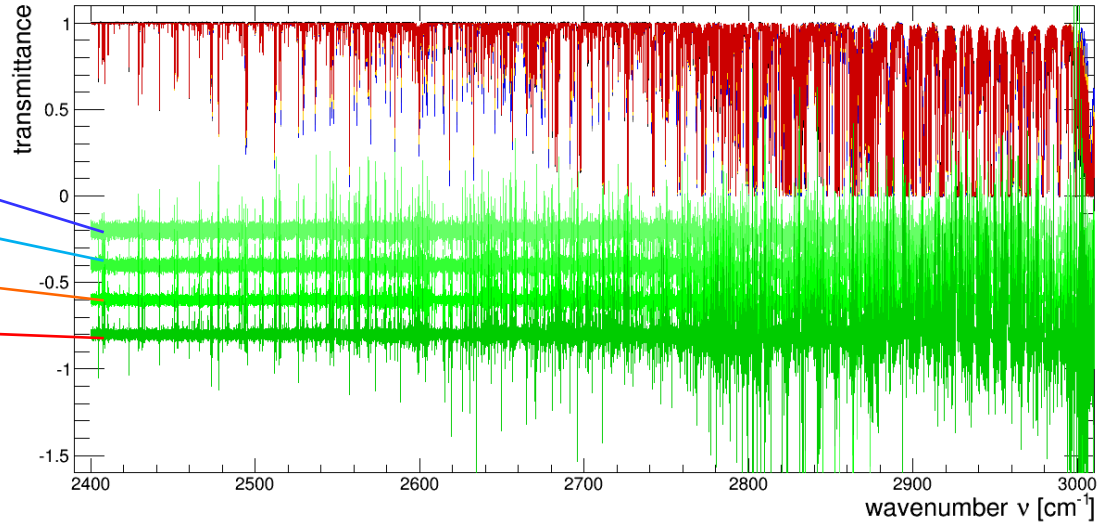
	MW 1	MW 2	MW 3	MW 4	MW 5	MW 6
CH_4 RT	✓	✓	✓	✓	✓	✓
Air + CH_4 RT	✓	✓	✓	✓	✓	✓
CH_4 Temp.	✓	✓	✓	✓	✓	✓
Air + CH_4 Temp.						
30 mbar	✓	✓	✓	✓	✓	✓
100 mbar	✓	✓	✓	✓	✓ ?	✓ ?
300 mbar						
1000 mbar						

Air Broadened Spectra (Mixture with 0.5% CH_4)

- Temperature dependence

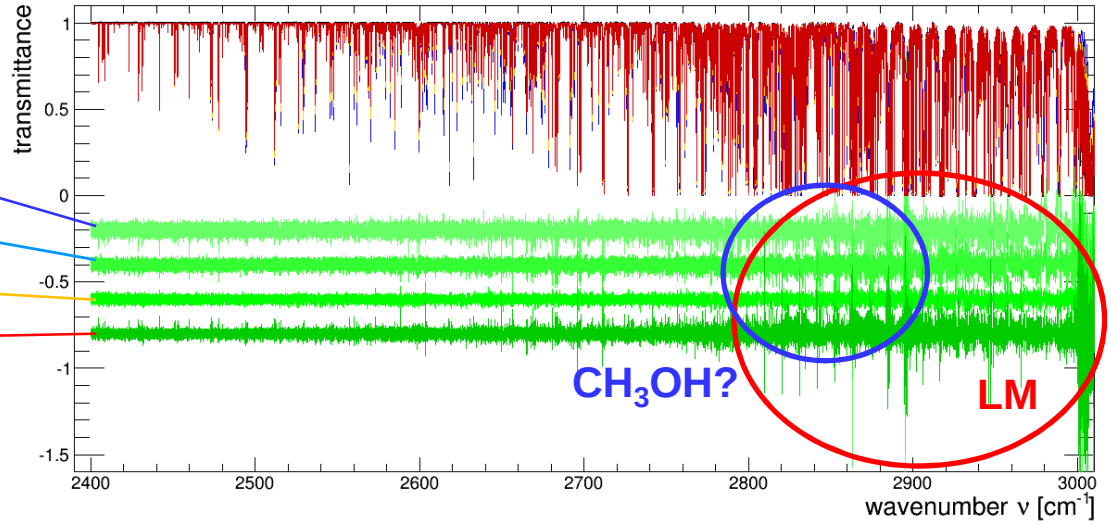
HITRAN 2012

300 mbar (223K)
300 mbar (248K)
300 mbar (296K)
300 mbar (333K)



New Line List 2015

300 mbar (223K)
300 mbar (248K)
300 mbar (296K)
300 mbar (333K)



NDACC Microwindows (Mix, Various Temperatures)

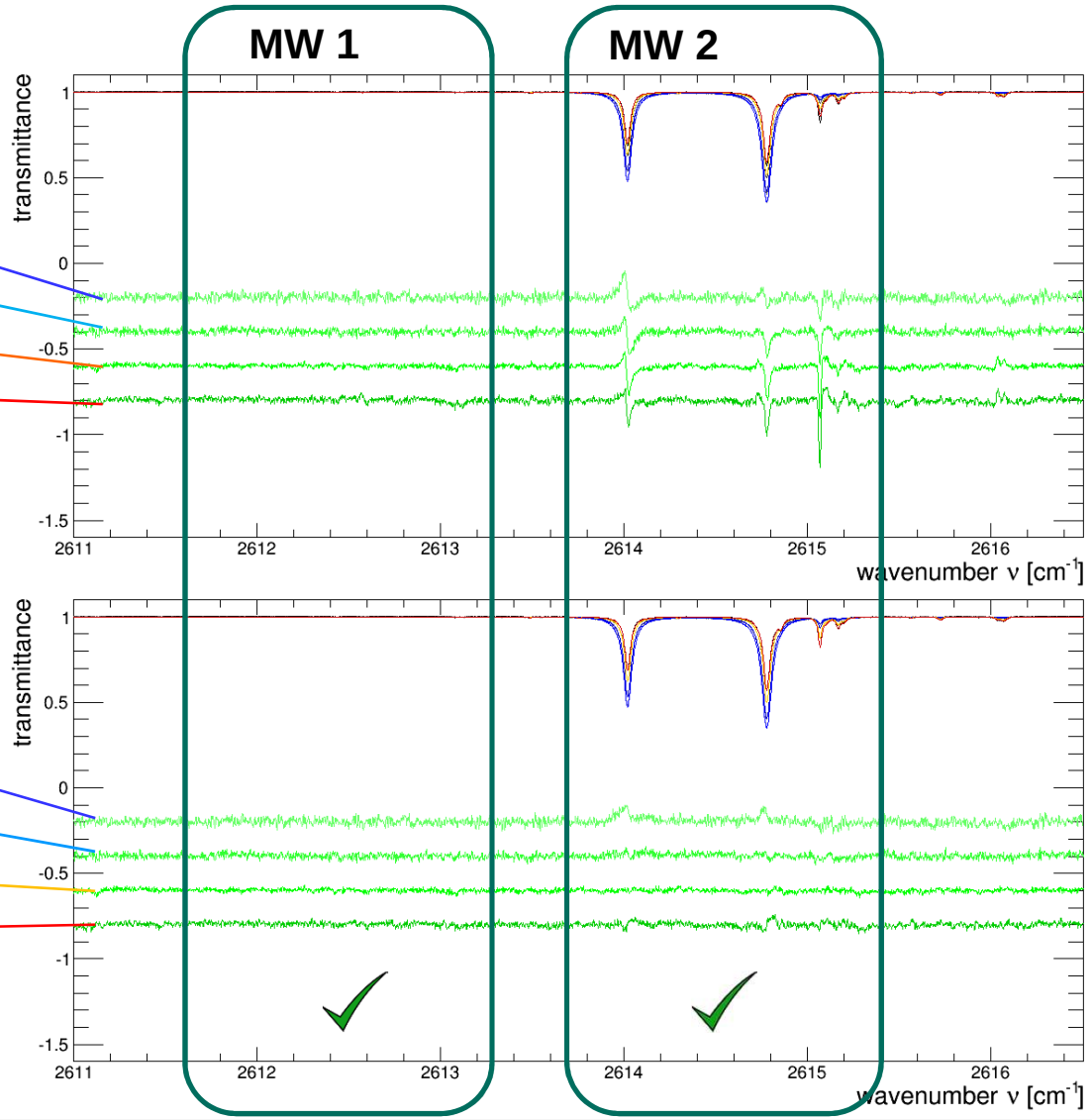
- **MW 1**: 2611.6 – 2613.3 cm^{-1}
- **MW 2**: 2613.7 – 2615.4 cm^{-1}

HITRAN 2012

300 mbar (223K)
300 mbar (248K)
300 mbar (296K)
300 mbar (333K)

New Line List 2015

300 mbar (223K)
300 mbar (248K)
300 mbar (296K)
300 mbar (333K)



NDACC Microwindows (Mix, Various Temperatures)

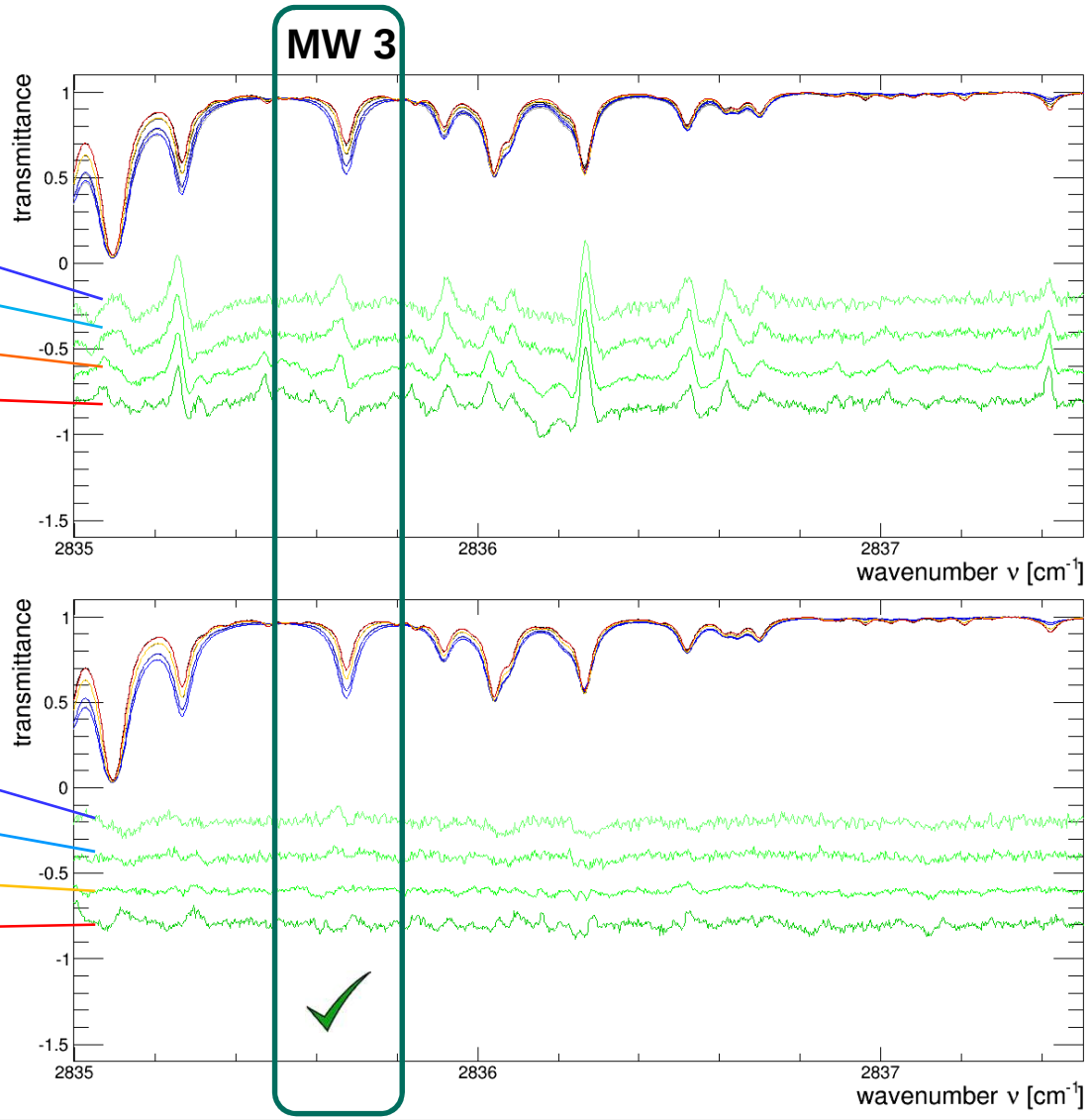
- **MW 3**: 2835.5 – 2835.8 cm^{-1}

HITRAN 2012

300 mbar (223K)
300 mbar (248K)
300 mbar (296K)
300 mbar (333K)

New Line List 2015

300 mbar (223K)
300 mbar (248K)
300 mbar (296K)
300 mbar (333K)



NDACC Microwindows (Mix, Various Temperatures)

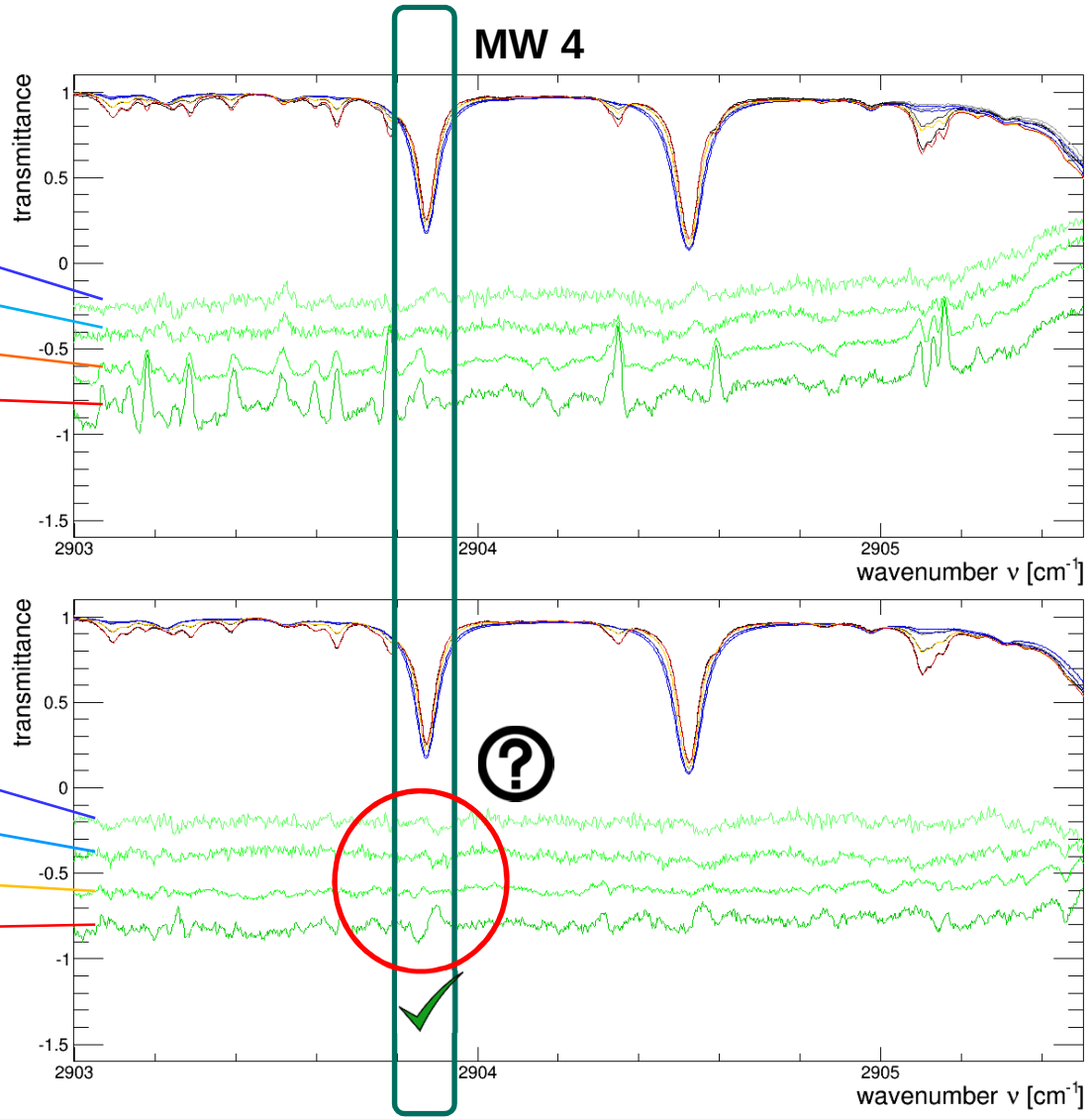
- **MW 4**: 2903.8 – 2903.9 cm^{-1}

HITRAN 2012

300 mbar (223K)
300 mbar (248K)
300 mbar (296K)
300 mbar (333K)

New Line List 2015

300 mbar (223K)
300 mbar (248K)
300 mbar (296K)
300 mbar (333K)



NDACC Microwindows (Mix, Various Temperatures)

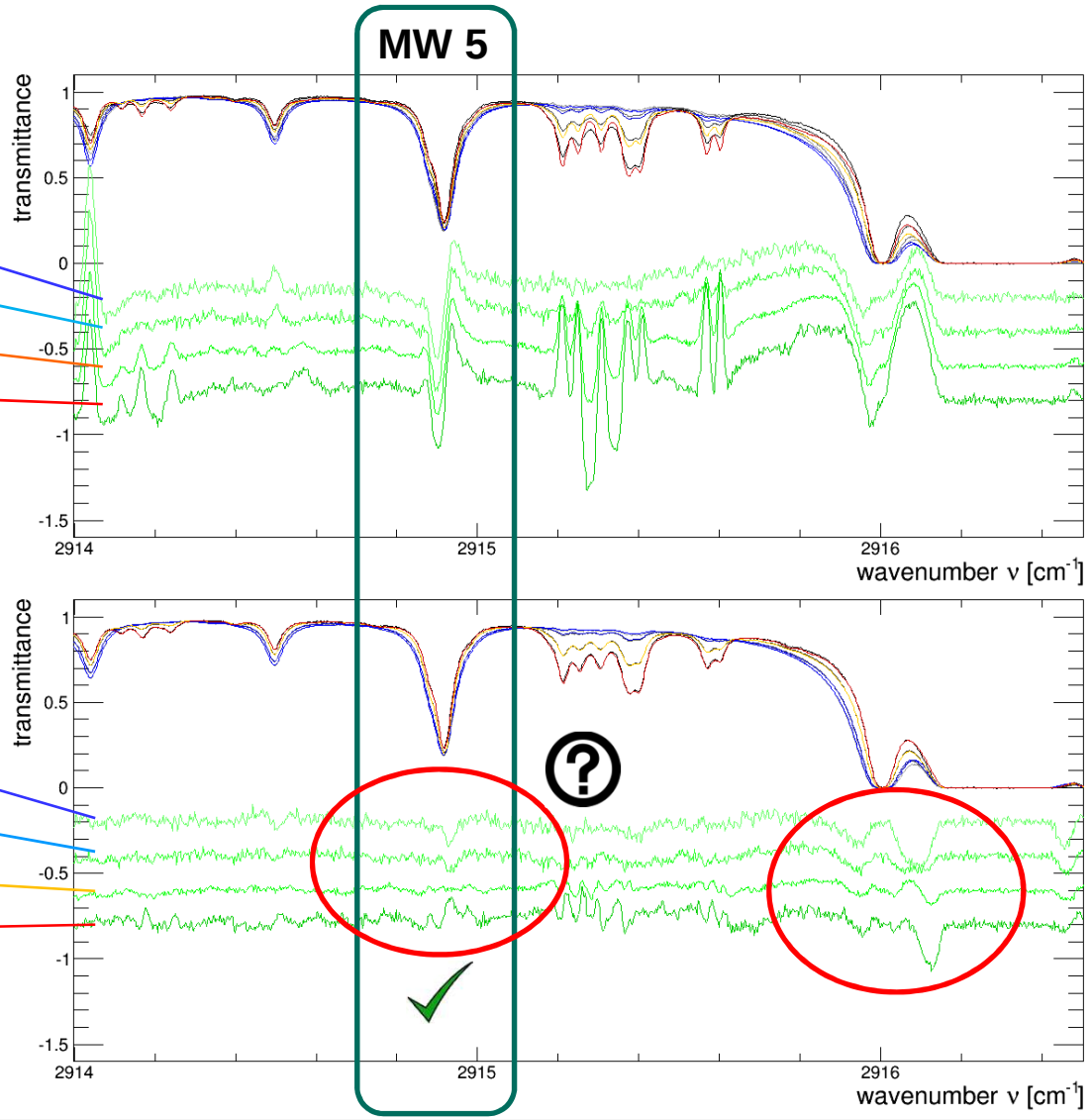
- **MW 5**: 2914.7 – 2915.1 cm^{-1}

HITRAN 2012

300 mbar (223K)
300 mbar (248K)
300 mbar (296K)
300 mbar (333K)

New Line List 2015

300 mbar (223K)
300 mbar (248K)
300 mbar (296K)
300 mbar (333K)



NDACC Microwindows (Mix, Various Temperatures)

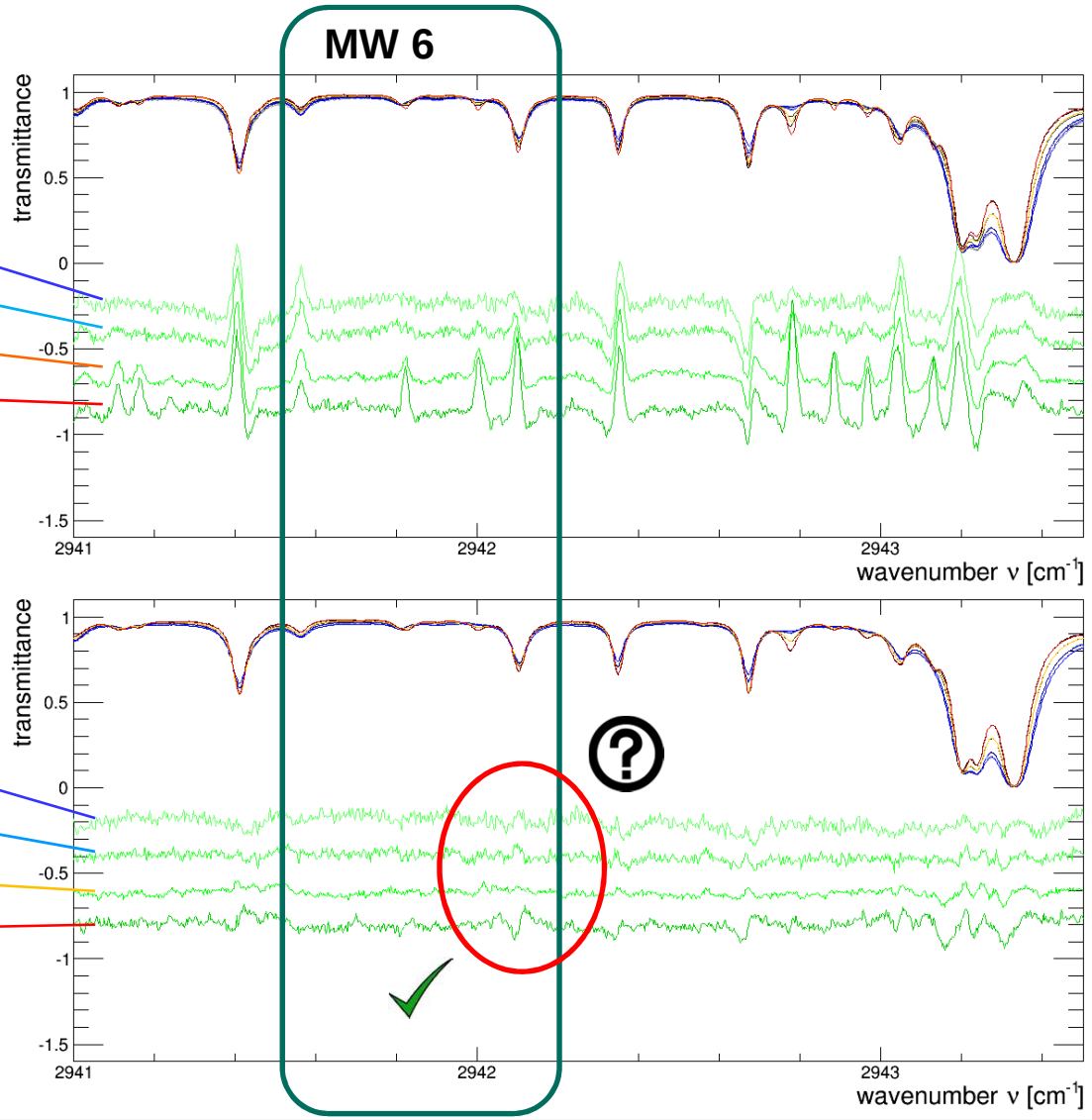
- **MW 6**: 2941.5 – 2942.2 cm^{-1}

HITRAN 2012

300 mbar (223K)
300 mbar (248K)
300 mbar (296K)
300 mbar (333K)

New Line List 2015

300 mbar (223K)
300 mbar (248K)
300 mbar (296K)
300 mbar (333K)



Overview

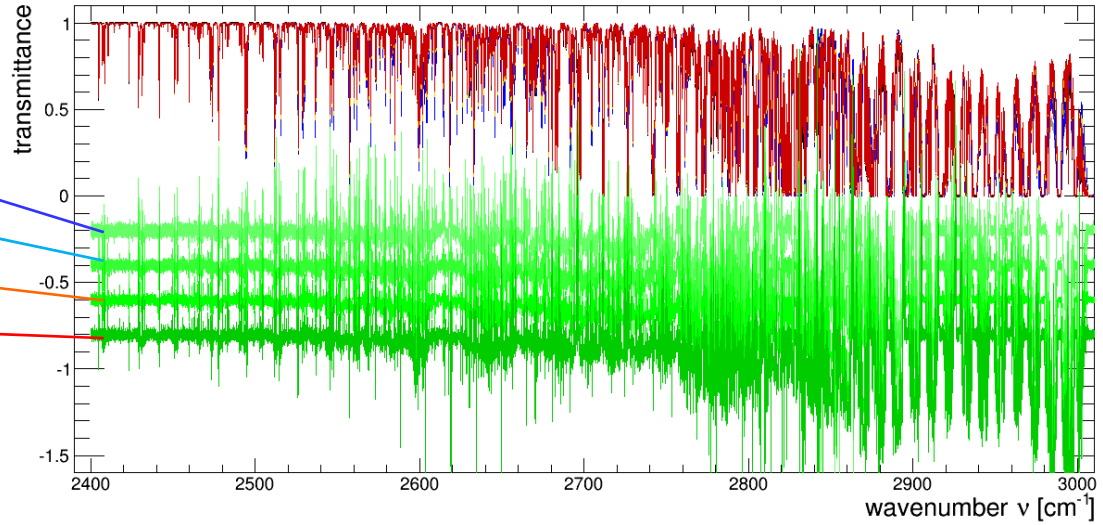
	MW 1	MW 2	MW 3	MW 4	MW 5	MW 6
CH_4 RT	✓	✓	✓	✓	✓	✓
Air+CH_4 RT	✓	✓	✓	✓	✓	✓
CH_4 Temp.	✓	✓	✓	✓	✓	✓
Air+CH_4 Temp.						
30 mbar	✓	✓	✓	✓	✓	✓
100 mbar	✓	✓	✓	✓	✓ ?	✓ ?
300 mbar	✓	✓	✓	✓ ?	✓ ?	✓ ?
1000 mbar						

Air Broadened Spectra (Mixture with 0.5% CH_4)

- Temperature dependence

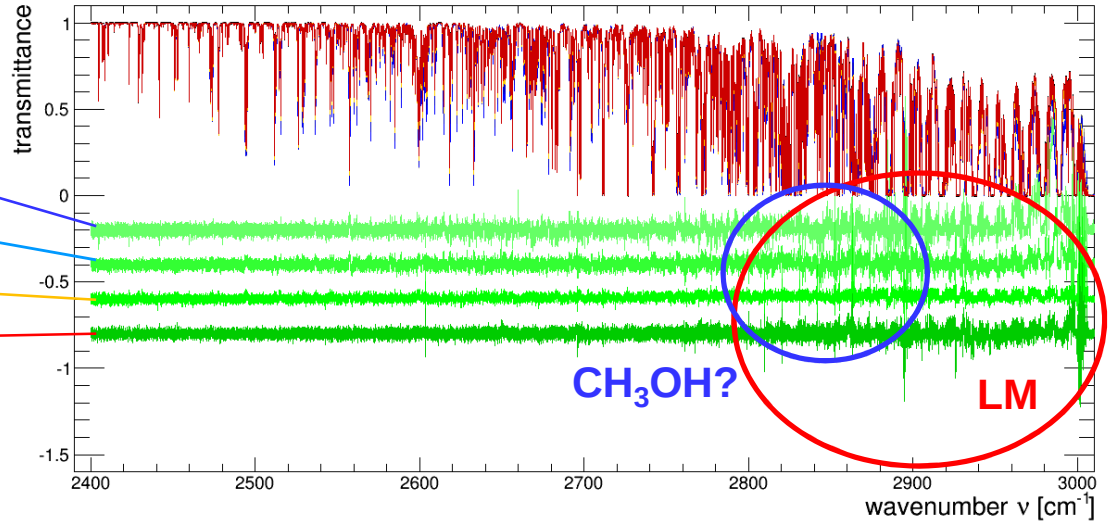
HITRAN 2012

1000 mbar (223K)
1000 mbar (258K)
1000 mbar (296K)
1000 mbar (313K)



New Line List 2015

1000 mbar (223K)
1000 mbar (258K)
1000 mbar (296K)
1000 mbar (313K)



NDACC Microwindows (Mix, Various Temperatures)

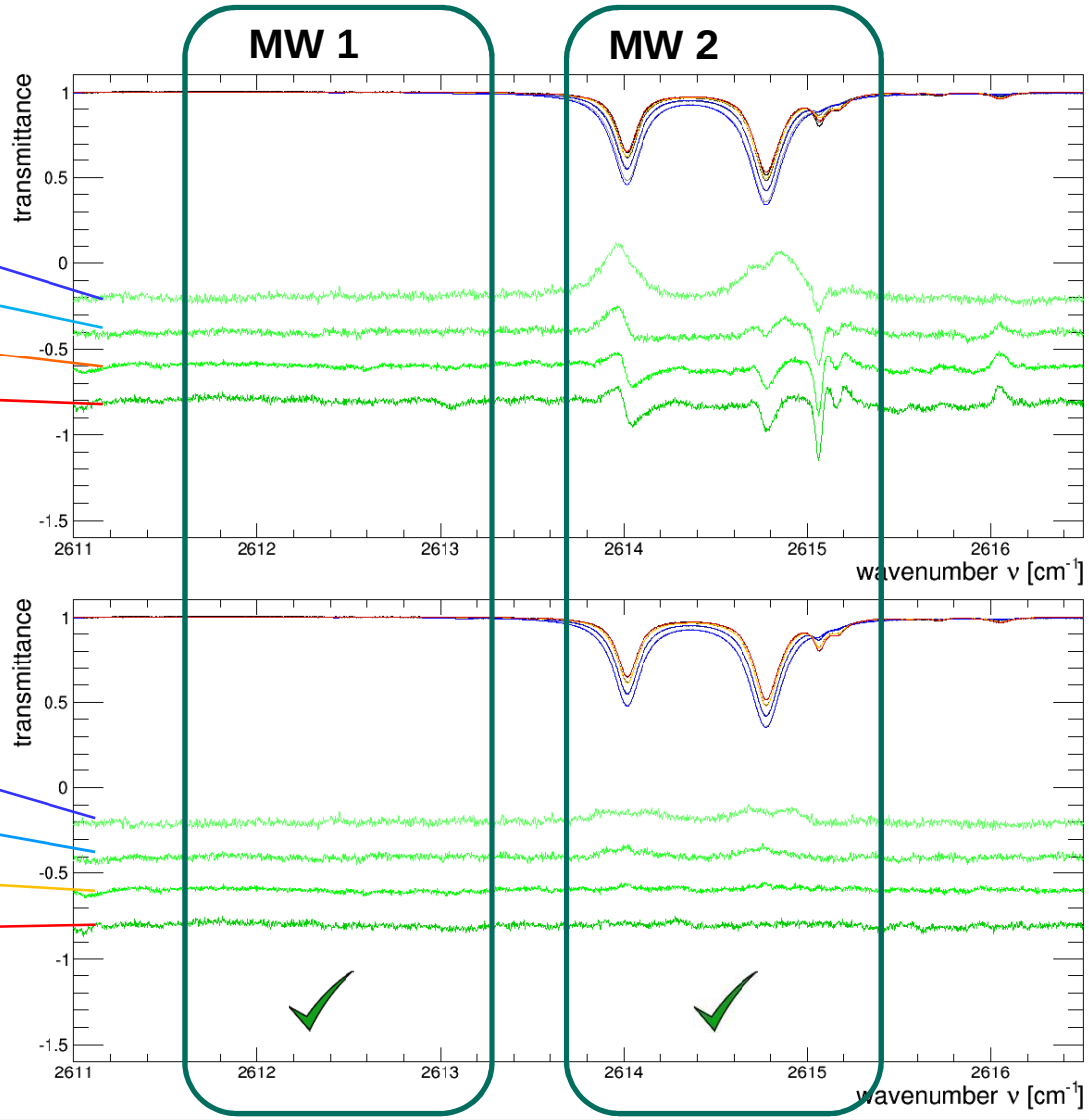
- **MW 1**: 2611.6 – 2613.3 cm^{-1}
- **MW 2**: 2613.7 – 2615.4 cm^{-1}

HITRAN 2012

1000 mbar (223K)
1000 mbar (258K)
1000 mbar (296K)
1000 mbar (313K)

New Line List 2015

1000 mbar (223K)
1000 mbar (258K)
1000 mbar (296K)
1000 mbar (313K)



NDACC Microwindows (Mix, Various Temperatures)

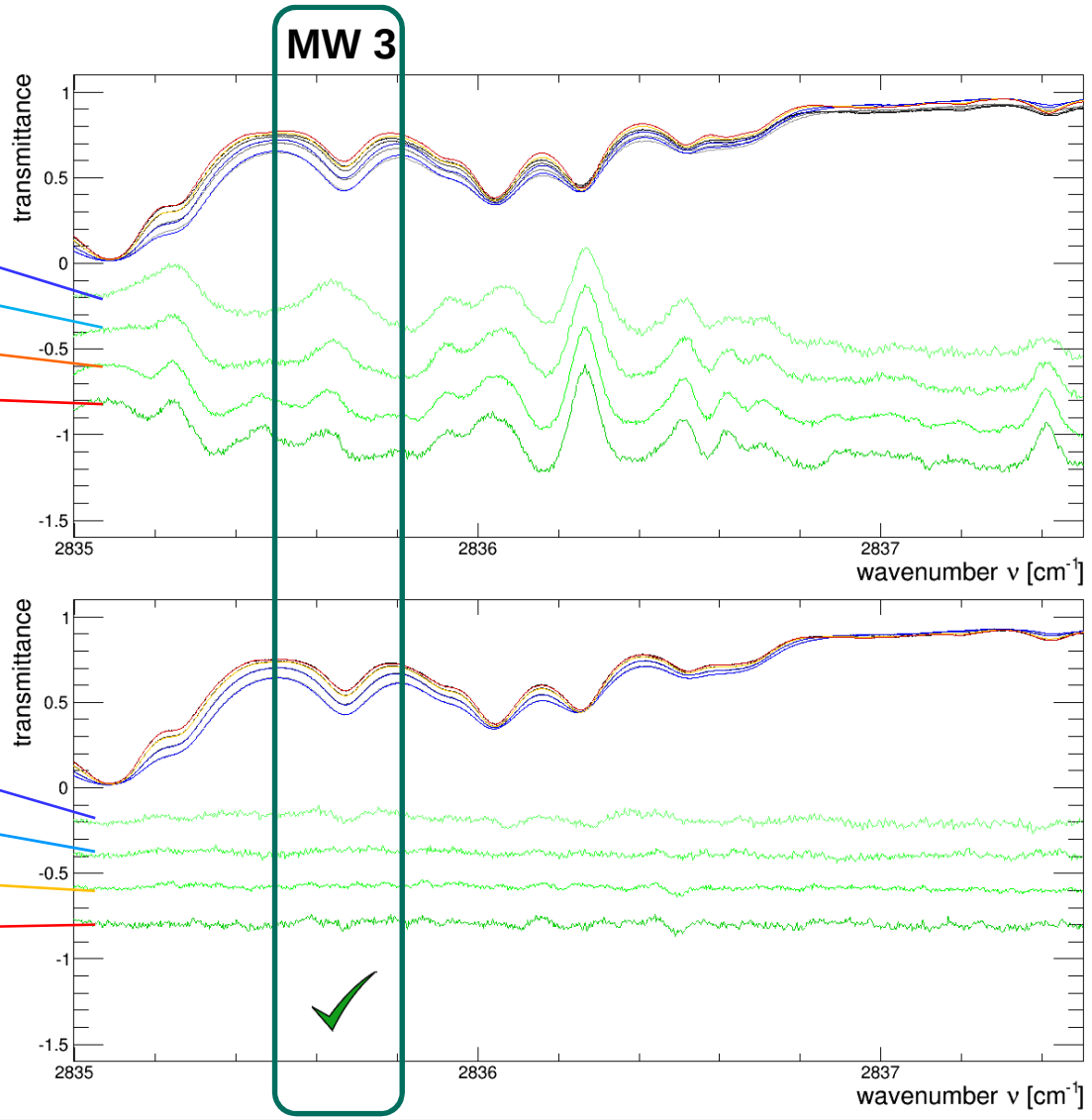
- **MW 3**: 2835.5 – 2835.8 cm^{-1}

HITRAN 2012

1000 mbar (223K)
1000 mbar (258K)
1000 mbar (296K)
1000 mbar (313K)

New Line List 2015

1000 mbar (223K)
1000 mbar (258K)
1000 mbar (296K)
1000 mbar (313K)



NDACC Microwindows (Mix, Various Temperatures)

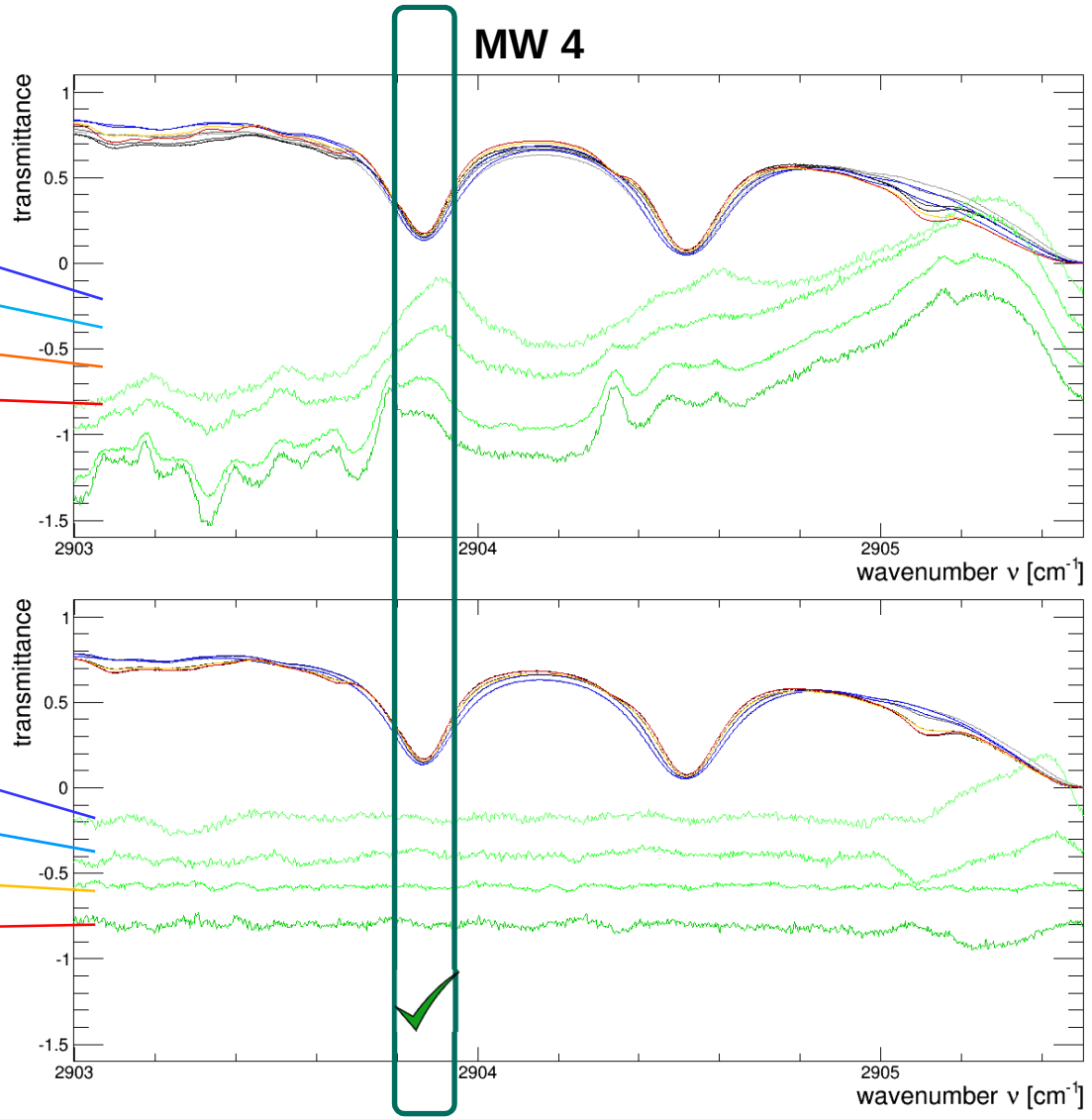
- **MW 4**: 2903.8 – 2903.9 cm^{-1}

HITRAN 2012

1000 mbar (223K)
1000 mbar (258K)
1000 mbar (296K)
1000 mbar (313K)

New Line List 2015

1000 mbar (223K)
1000 mbar (258K)
1000 mbar (296K)
1000 mbar (313K)



NDACC Microwindows (Mix, Various Temperatures)

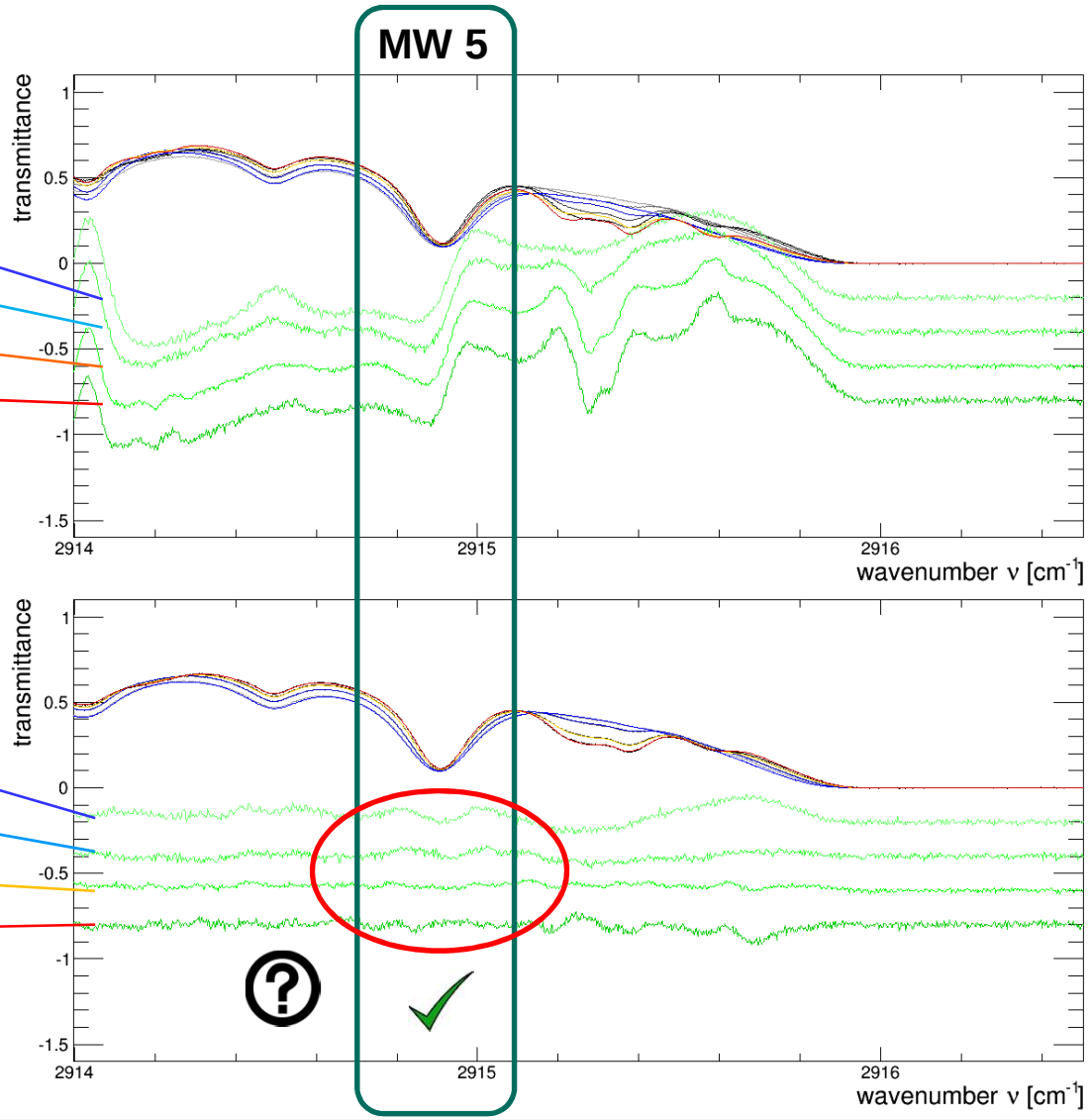
- **MW 5**: 2914.7 – 2915.1 cm^{-1}

HITRAN 2012

1000 mbar (223K)
1000 mbar (258K)
1000 mbar (296K)
1000 mbar (313K)

New Line List 2015

1000 mbar (223K)
1000 mbar (258K)
1000 mbar (296K)
1000 mbar (313K)



NDACC Microwindows (Mix, Various Temperatures)

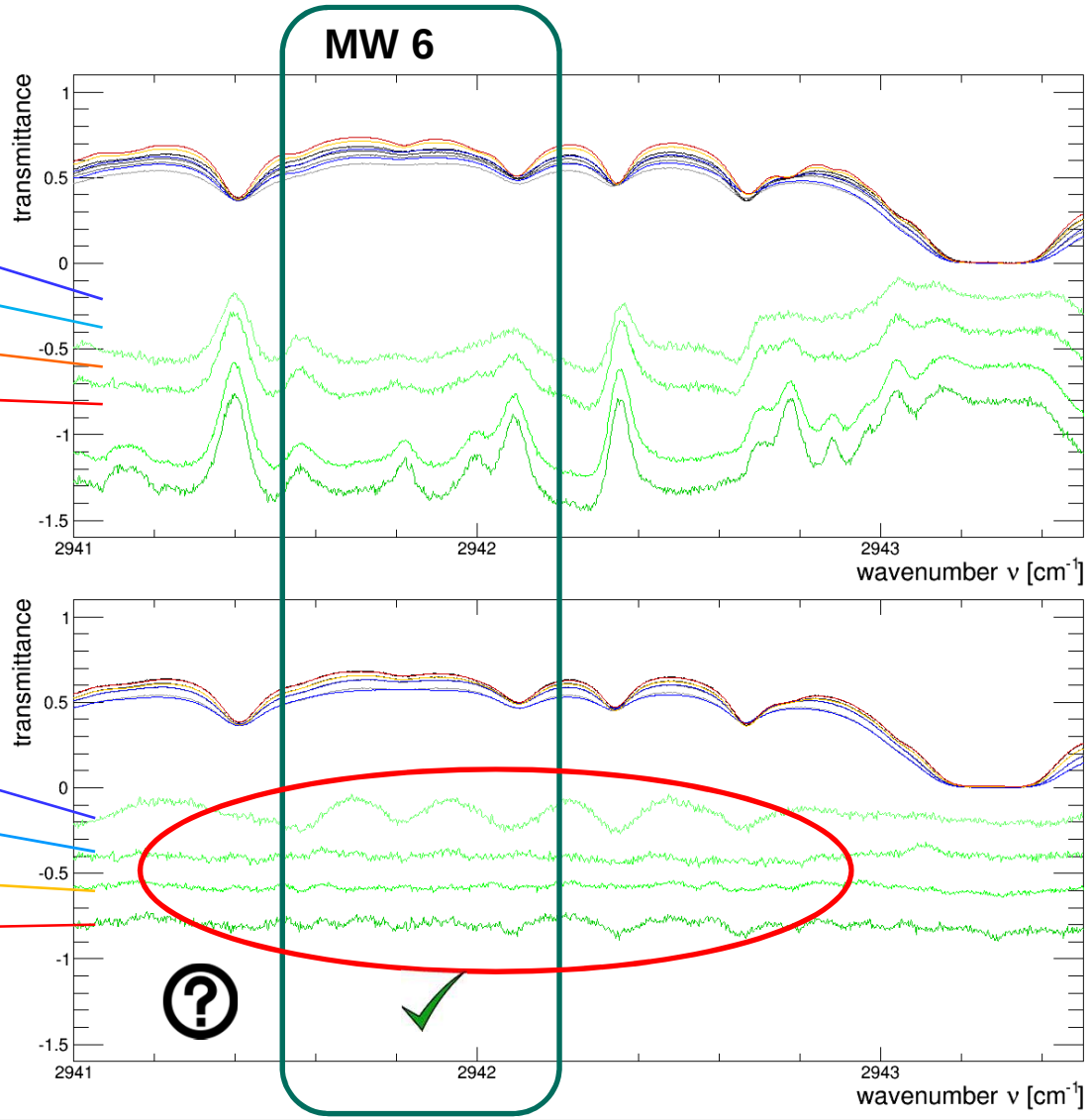
- **MW 6**: 2941.5 – 2942.2 cm^{-1}

HITRAN 2012

1000 mbar (223K)
1000 mbar (258K)
1000 mbar (296K)
1000 mbar (313K)

New Line List 2015

1000 mbar (223K)
1000 mbar (258K)
1000 mbar (296K)
1000 mbar (313K)



Overview

	MW 1	MW 2	MW 3	MW 4	MW 5	MW 6
CH_4 RT	✓	✓	✓	✓	✓	✓
Air+CH_4 RT	✓	✓	✓	✓	✓	✓
CH_4 Temp.	✓	✓	✓	✓	✓	✓
Air+CH_4 Temp.	✓	✓	✓	✓	✓	✓
30 mbar	✓	✓	✓	✓	✓	✓
100 mbar	✓	✓	✓	✓	✓ ?	✓
300 mbar	✓	✓	✓	✓ ?	✓ ?	✓ ?
1000 mbar	✓	✓	✓	✓	✓ ?	✓ ?

Summary & Outlook

- Measurements DLR[1] (self and air broadened spectra)
- Multispectrum line parameter fitting software developed
- Room temperature self broadened and air broadened spectra have been processed from 2400 to 3000 cm^{-1}
- Temperature dependence of line parameters have been deduced from low and high temperature spectra
- Consolidated line list for the complete range (2400 to 3000 cm^{-1}) is now available (New Line List 2015, Preliminary Line List 2012)
- TO DO: Make a To-Do List! Strong Line Mixing (Line Clusters)? Temperature Dependence?
- TO DO: Make a To-Do List! Number of Parameters should be reduced?
- TO DO: Make a To-Do List! Lower State Energy (E'') could be fitted as well?

Acknowledgement: this work is supported by DFG[2] (project HA 6190/1-1)

1. DLR Deutsches Zentrum für Luft- und Raumfahrt / German Aerospace Center, Oberpfaffenhofen, Germany
2. DFG Deutsche Forschungsgemeinschaft / German Research Foundation