Empirical Pseudo-Line-List for Isoprene (C_5H_8)

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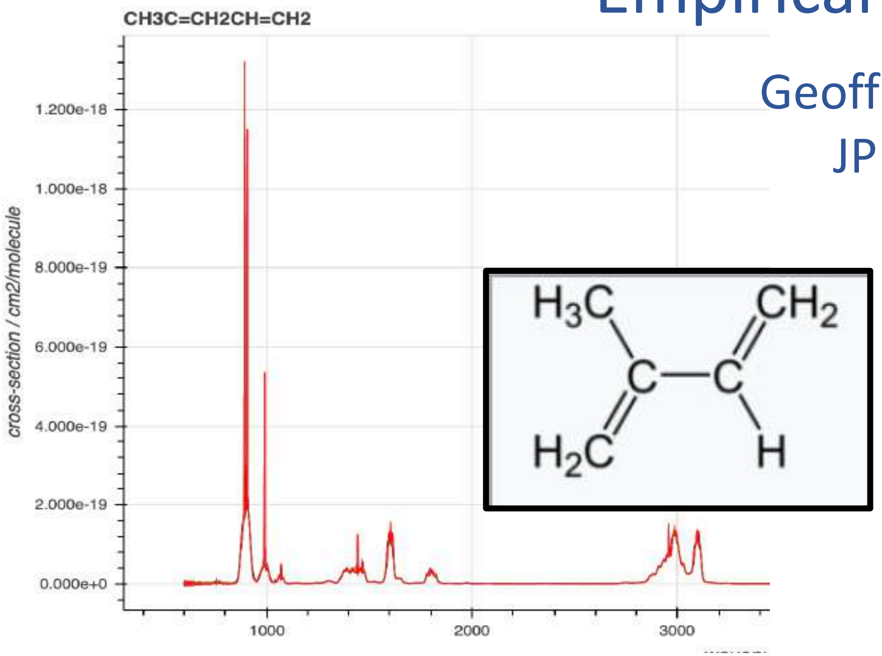
2020-02-13



Isoprene has three conformers. The s-trans, shown left and right (a), accounts for 98% of isoprene at room T.

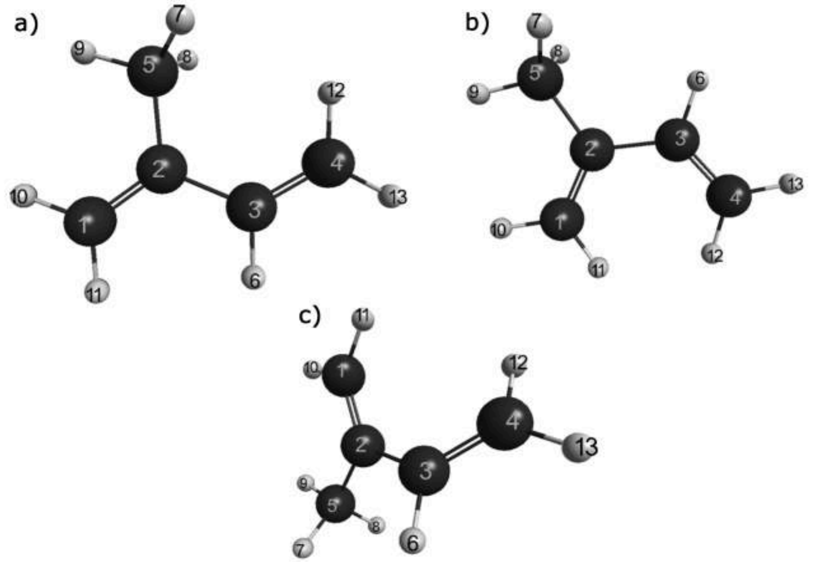
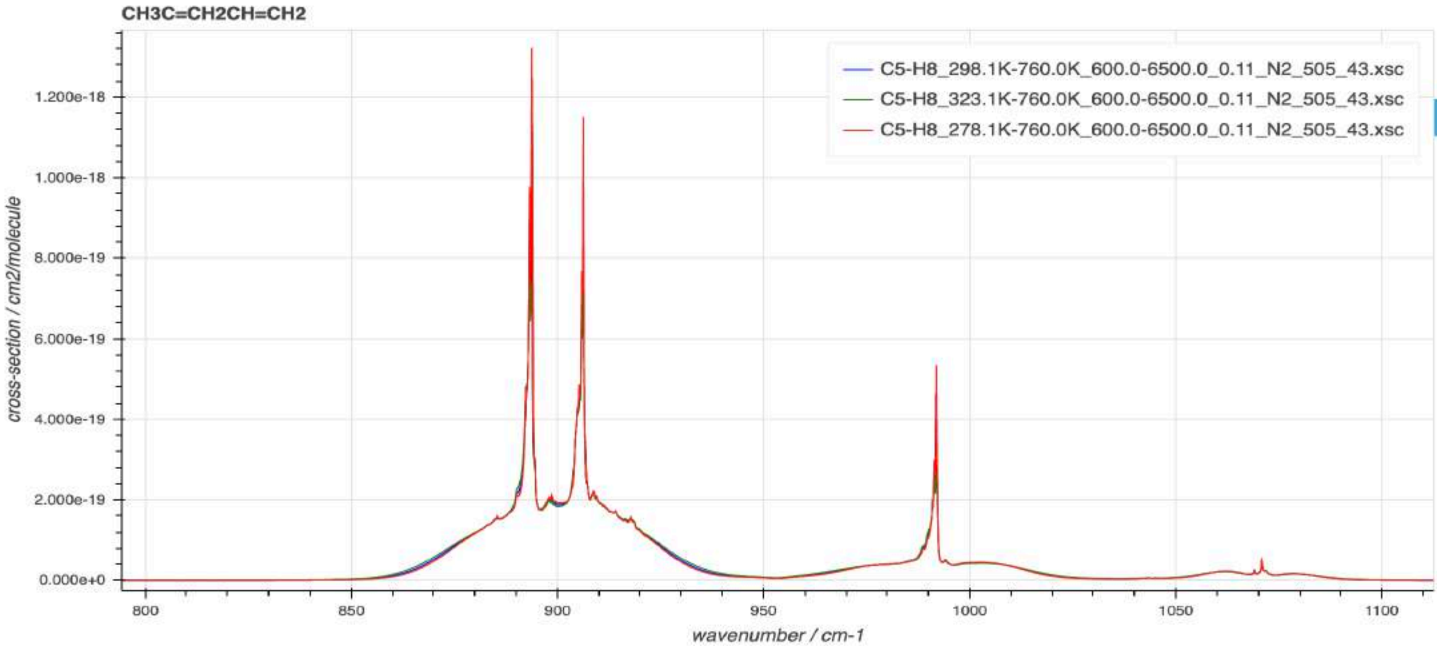


Figure 2. Isoprene in the planar s-*trans* **(a)** and s-*cis* **(b)** conformations. The gauche s-*cis* conformation is shown in **(c)**, with the dihedral angle, C1-C2-C3-C4 = 35°, corresponding to the structure calculated by Squillacote and Liang (2005) using the G3B3 method.

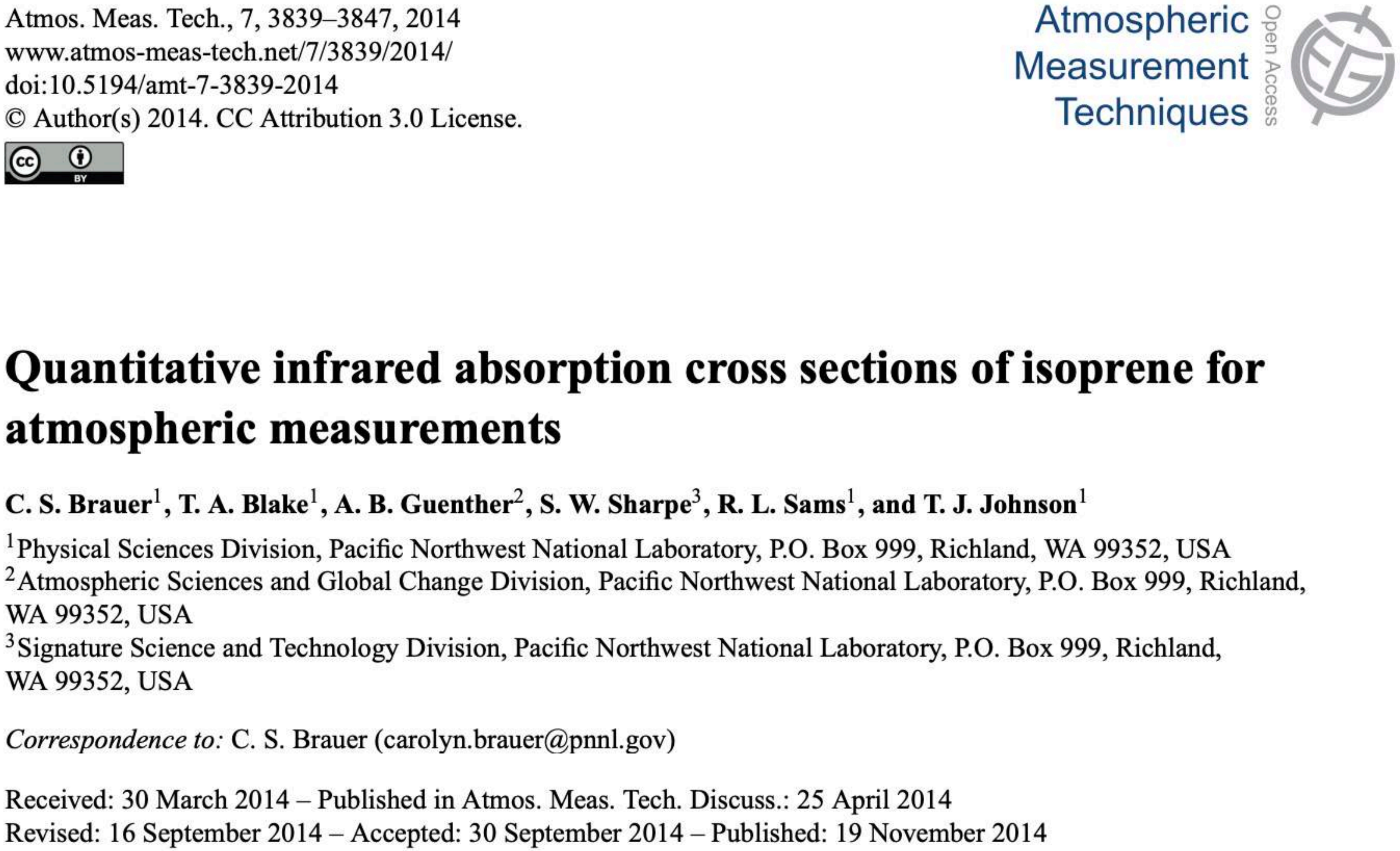


Strongest and sharpest absorption features lie between 850-1000 $cm^{-1.}$ The peaks at 894, 906, and 992 cm^{-1} correspond to the ν_{28}, ν_{27}, and ν_{26} absorption bands, look like the best candidates for isoprene measurements.

Isoprene Laboratory Spectra from PNNL

The PNNL (Brauer et al., 2014) cross-sections were down-loaded from the HITRAN website and converted into representative transmittance spectra.

PNNL spectra cover 600-6000 cm^{-1}
at 0.06 cm^{-1} resolution



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Atmospheric
Measurement
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Quantitative infrared absorption cross sections of isoprene for atmospheric measurements

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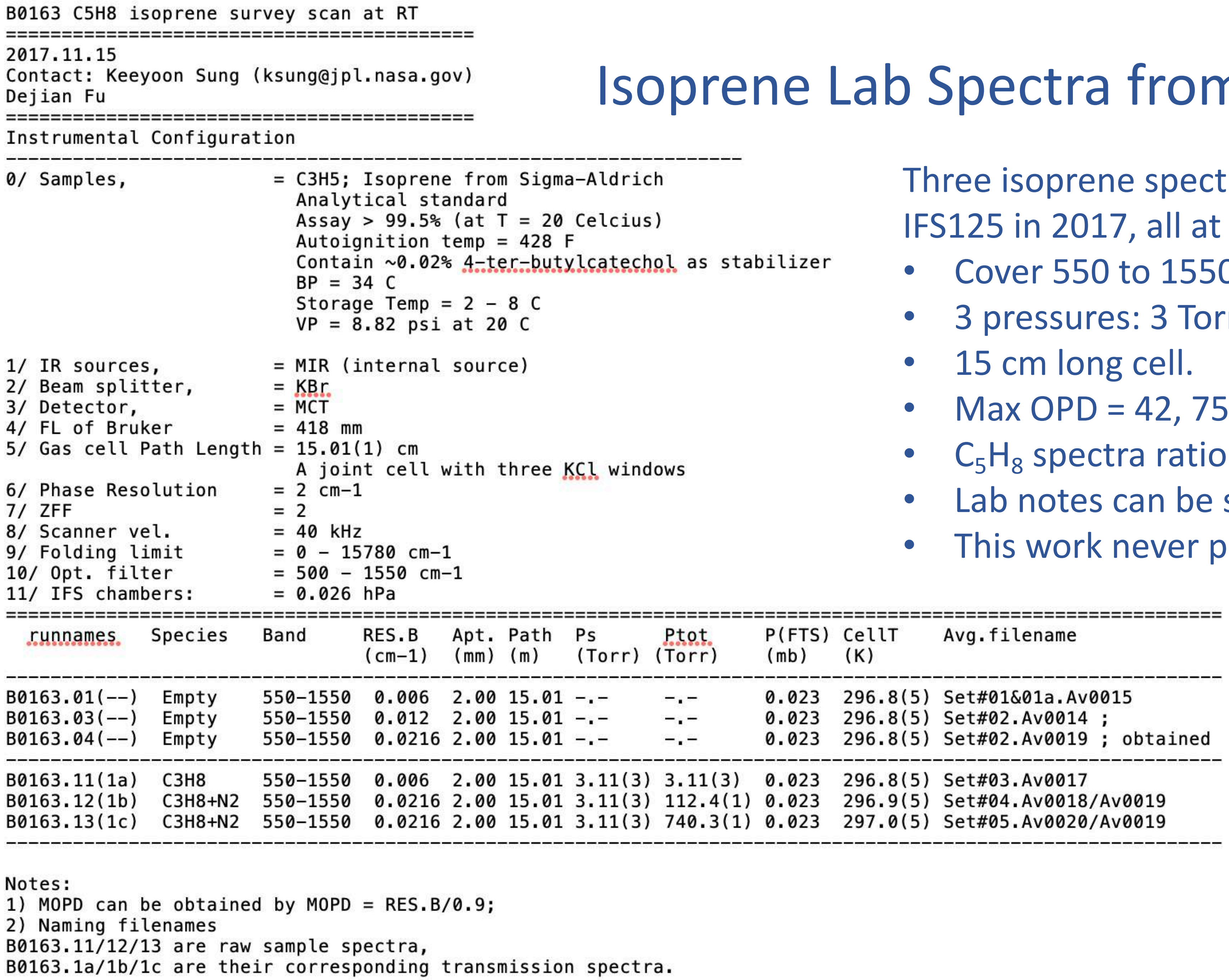
Isoprene Lab Spectra from JPL (Keeyoon Sung)



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B0163 C5H8 isoprene survey scan at RT
==========================================
2017.11.15
Contact: Keeyoon Sung (ksung@jpl.nasa.gov)
Dejian Fu
==========================================
Instrumental Configuration
--------------------------------------------------------------------
0/ Samples,               = C3H5; Isoprene from Sigma-Aldrich
                            Analytical standard
                            Assay > 99.5% (at T = 20 Celcius)
                            Autoignition temp = 428 F
                            Contain ~0.02% 4-ter-butylcatechol as stabilizer
                            BP = 34 C
                            Storage Temp = 2 - 8 C
                            VP = 8.82 psi at 20 C

1/ IR sources,            = MIR (internal source)
2/ Beam splitter,         = KBr
3/ Detector,              = MCT
4/ FL of Bruker           = 418 mm
5/ Gas cell Path Length = 15.01(1) cm
                            A joint cell with three KCl windows
6/ Phase Resolution       = 2 cm-1
7/ ZFF                    = 2
8/ Scanner vel.           = 40 kHz
9/ Folding limit          = 0 - 15780 cm-1
10/ Opt. filter           = 500 - 1550 cm-1
11/ IFS chambers:         = 0.026 hPa
===============================================================================================================
  runnames    Species    Band      RES.B   Apt. Path   Ps       Ptot     P(FTS) CellT     Avg.filename
                                  (cm-1)  (mm) (m)    (Torr)  (Torr)    (mb)   (K)
---------------------------------------------------------------------------------------------------------------
B0163.01(--)  Empty     550-1550  0.006   2.00 15.01 -.-      -.-       0.023  296.8(5) Set#01&01a.Av0015
B0163.03(--)  Empty     550-1550  0.012   2.00 15.01 -.-      -.-       0.023  296.8(5) Set#02.Av0014 ;
B0163.04(--)  Empty     550-1550  0.0216 2.00 15.01 -.-      -.-       0.023  296.8(5) Set#02.Av0019 ; obtained
---------------------------------------------------------------------------------------------------------------
B0163.11(1a)  C3H8      550-1550  0.006   2.00 15.01 3.11(3) 3.11(3)   0.023  296.8(5) Set#03.Av0017
B0163.12(1b)  C3H8+N2   550-1550  0.0216 2.00 15.01 3.11(3) 112.4(1) 0.023  296.9(5) Set#04.Av0018/Av0019
B0163.13(1c)  C3H8+N2   550-1550  0.0216 2.00 15.01 3.11(3) 740.3(1) 0.023  297.0(5) Set#05.Av0020/Av0019
---------------------------------------------------------------------------------------------------------------

Notes:
1) MOPD can be obtained by MOPD = RES.B/0.9;
2) Naming filenames
B0163.11/12/13 are raw sample spectra,
B0163.1a/1b/1c are their corresponding transmission spectra.
```

Three isoprene spectra measured by the JPL Lab Bruker IFS125 in 2017, all at 297K.

- Cover 550 to 1550 cm^{-1} - up to 0.006 cm^{-1} resolution
- 3 pressures: 3 Torr (pure); 112 Torr, & 740 Torr
- 15 cm long cell.
- Max OPD = 42, 75, or 150 cm, depending on P
- C_5H_8 spectra ratioed by empty cell spectrum
- Lab notes can be seen on left
- This work never published

Partition Functions

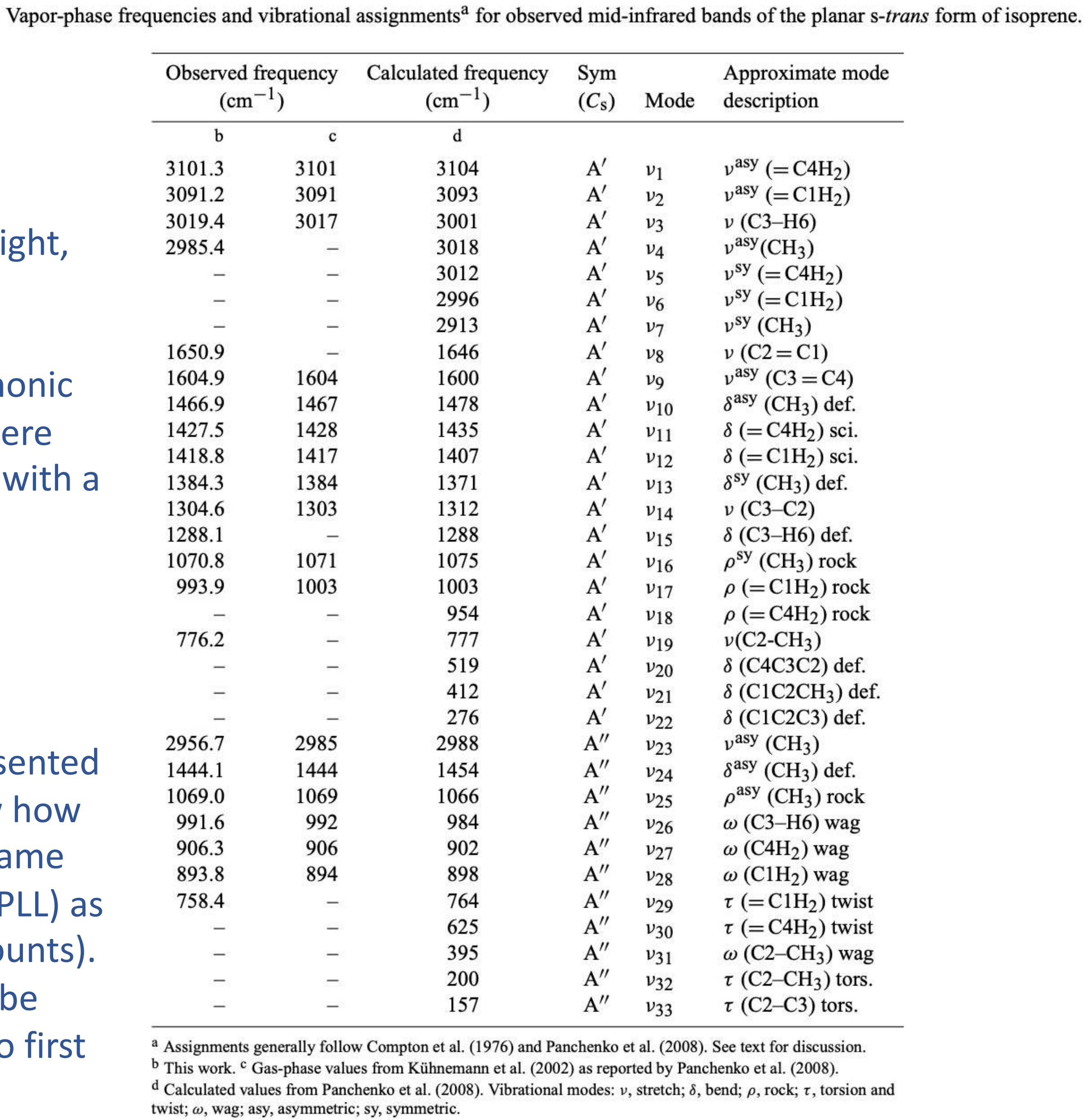
Isoprene (C_5H_8) has N=13 atoms and therefore 3N-6 = 33 vibrational modes. These 33 are listed in the table on the right, taken from Brauer et al. (2014). None are degenerate.

In generating the EPLL, isoprene was assumed to be a harmonic oscillator and so all 33 of the fundamental wavenumbers were used in computing the vibrational partition function, along with a rotational partition function ratio of

$$Q_R(T_0)/Q_R(T) = (T_0/T)^{\beta}$$

with the exponent, β =2.0, being approximated due to the torsional bands (diatomic β = 1.0; poly-atomic β = 1.5).

The low-wavenumber torsional modes will be poorly represented by this harmonic oscillator approximation, but I don't know how to evaluate a better approximation. In any case, since the same error will be made in fitting the lab spectra (to derive the EPLL) as in fitting the atmospheric spectra (to retrieve isoprene amounts). So any shortcoming of the adopted partition functions will be accommodated by the E"s of the EPLL and thereby cancel to first order, at least for temperatures between 278 and 323K.



Vapor-phase frequencies and vibrational assignments[a] for observed mid-infrared bands of the planar s-*trans* form of isoprene.

Observed frequency (cm^{-1})		Calculated frequency (cm^{-1})	Sym (C_s)	Mode	Approximate mode description
b	c	d			
3101.3	3101	3104	A′	ν_1	ν^{asy} (=C4H$_2$)
3091.2	3091	3093	A′	ν_2	ν^{asy} (=C1H$_2$)
3019.4	3017	3001	A′	ν_3	ν (C3–H6)
2985.4	–	3018	A′	ν_4	ν^{asy}(CH$_3$)
–	–	3012	A′	ν_5	ν^{sy} (=C4H$_2$)
–	–	2996	A′	ν_6	ν^{sy} (=C1H$_2$)
–	–	2913	A′	ν_7	ν^{sy} (CH$_3$)
1650.9	–	1646	A′	ν_8	ν (C2=C1)
1604.9	1604	1600	A′	ν_9	ν^{asy} (C3=C4)
1466.9	1467	1478	A′	ν_{10}	δ^{asy} (CH$_3$) def.
1427.5	1428	1435	A′	ν_{11}	δ (=C4H$_2$) sci.
1418.8	1417	1407	A′	ν_{12}	δ (=C1H$_2$) sci.
1384.3	1384	1371	A′	ν_{13}	δ^{sy} (CH$_3$) def.
1304.6	1303	1312	A′	ν_{14}	ν (C3–C2)
1288.1	–	1288	A′	ν_{15}	δ (C3–H6) def.
1070.8	1071	1075	A′	ν_{16}	ρ^{sy} (CH$_3$) rock
993.9	1003	1003	A′	ν_{17}	ρ (=C1H$_2$) rock
–	–	954	A′	ν_{18}	ρ (=C4H$_2$) rock
776.2	–	777	A′	ν_{19}	ν(C2-CH$_3$)
–	–	519	A′	ν_{20}	δ (C4C3C2) def.
–	–	412	A′	ν_{21}	δ (C1C2CH$_3$) def.
–	–	276	A′	ν_{22}	δ (C1C2C3) def.
2956.7	2985	2988	A″	ν_{23}	ν^{asy} (CH$_3$)
1444.1	1444	1454	A″	ν_{24}	δ^{asy} (CH$_3$) def.
1069.0	1069	1066	A″	ν_{25}	ρ^{asy} (CH$_3$) rock
991.6	992	984	A″	ν_{26}	ω (C3–H6) wag
906.3	906	902	A″	ν_{27}	ω (C4H$_2$) wag
893.8	894	898	A″	ν_{28}	ω (C1H$_2$) wag
758.4	–	764	A″	ν_{29}	τ (=C1H$_2$) twist
–	–	625	A″	ν_{30}	τ (=C4H$_2$) twist
–	–	395	A″	ν_{31}	ω (C2–CH$_3$) wag
–	–	200	A″	ν_{32}	τ (C2–CH$_3$) tors.
–	–	157	A″	ν_{33}	τ (C2–C3) tors.

[a] Assignments generally follow Compton et al. (1976) and Panchenko et al. (2008). See text for discussion.

[b] This work. [c] Gas-phase values from Kühnemann et al. (2002) as reported by Panchenko et al. (2008).

[d] Calculated values from Panchenko et al. (2008). Vibrational modes: ν, stretch; δ, bend; ρ, rock; τ, torsion and twist; ω, wag; asy, asymmetric; sy, symmetric.

Direct retrieval of isoprene from satellite-based infrared measurements

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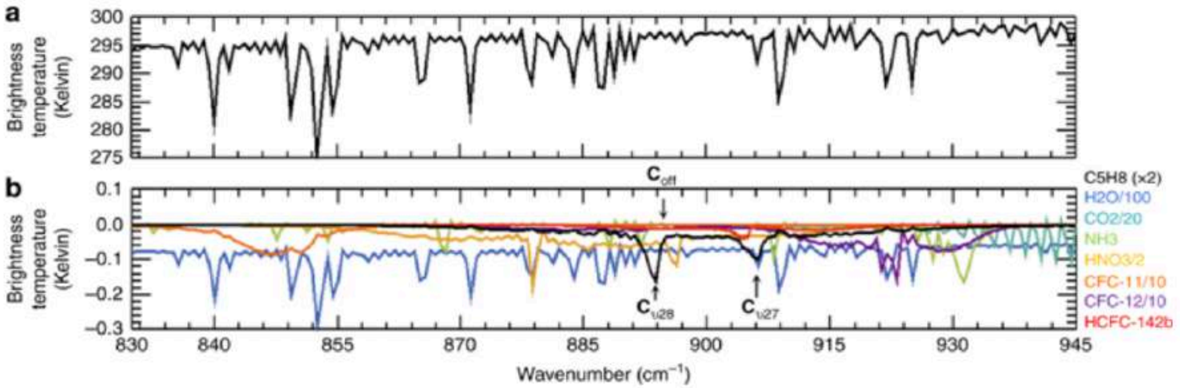
Nature Communications **10**, Article number: 3811 (2019) | Cite this article

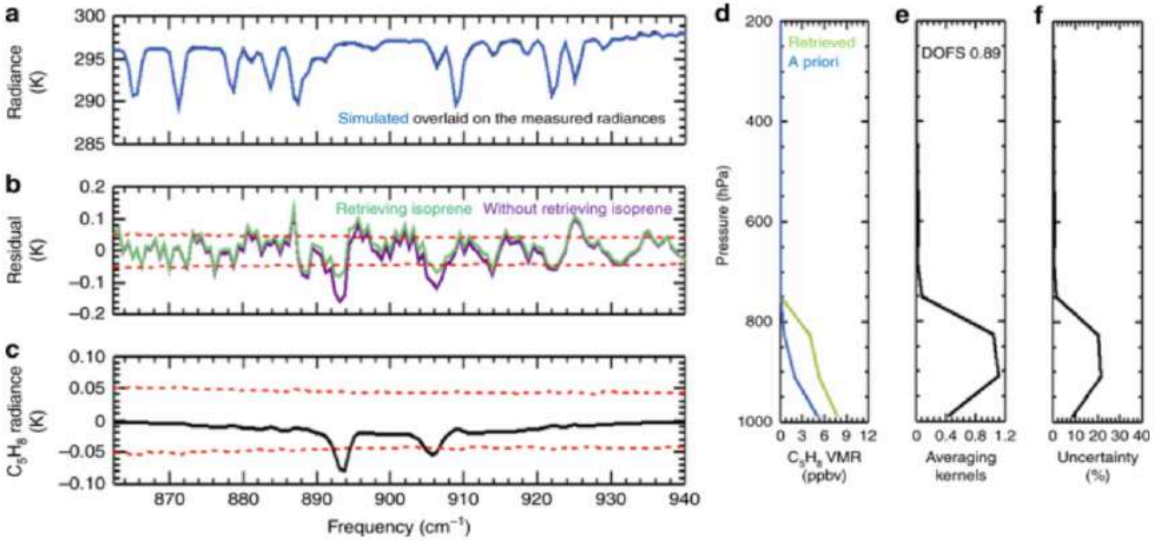
Fig. 1



Example CrIS spectrum and relevant speciated spectral features. **a** An individual CrIS-measured spectrum (black line) in the region of isoprene's ν_{27} and ν_{28} bands, obtained over Amazonia (8.698°S, 69.134°W) on September 30, 2014. The major features are associated with H_2O vapor. **b** Spectral contributions from isoprene (C_5H_8), water vapor (H_2O), carbon dioxide (CO_2), nitric acid (HNO_3), ammonia (NH_3), and chlorofluorocarbons (CFC-11 and CFC-12) for the same scene. $\mathbf{C}_{\nu 28}$: spectral channel near the peak of isoprene absorption for the ν_{28} band. $\mathbf{C}_{off}$: closest spectral channel to $\mathbf{C}_{\nu 28}$ that is near the continuum featuring no isoprene absorption. Spectral features for H_2O,

Fu et al. used the PNNL cross-sections directly, despite their covering only one pressure (1 atm) and 278 to 323K. But this is probably okay for the warm Amazonia PBL.

Fig. 4



An example CrIS isoprene retrieval over Amazonia (8.698°S, 69.134°W) on September 30, 2014. **a** Calculated (blue) spectrum overlaid on the CrIS-measured (black) spectrum, plotted in brightness temperature units. The major features are due to H_2O vapor. **b** Residual spectra (observed—calculated) after accounting for water vapor (H_2O), nitric acid (HNO_3), ammonia (NH_3), and relevant surface and cloud properties. The purple line indicates the residual spectrum before accounting for isoprene (C_5H_8), clearly showing the isoprene signals peaking at 893.75 cm^{-1} (ν_{28} band) and 906.25 cm^{-1} (ν_{27} band). The green line depicts the residuals after fitting for isoprene. The red dashed lines denote the single-pixel CrIS noise level as

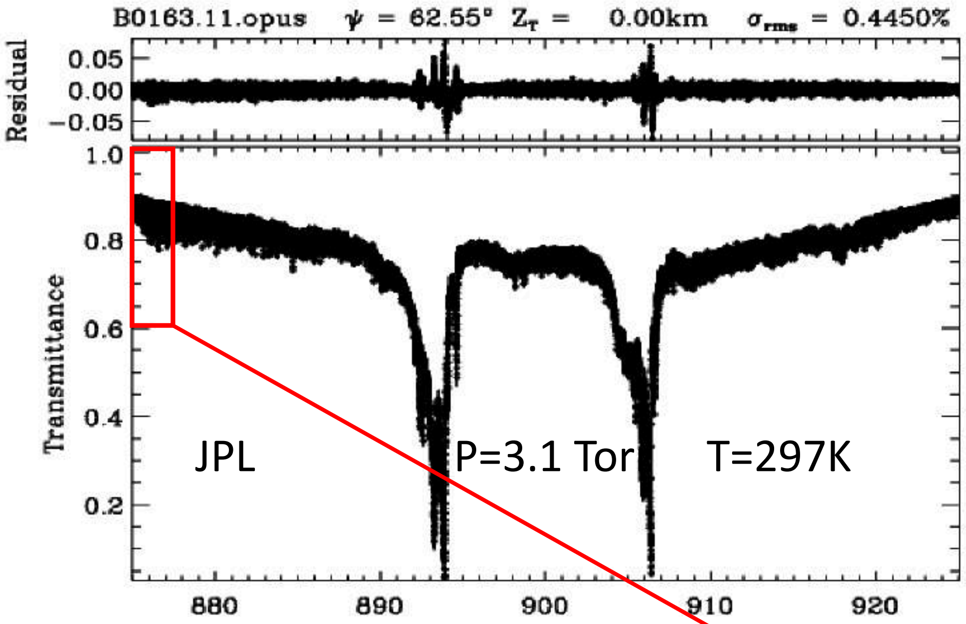
Fitted Windows

Ten windows were defined with boundaries at local minima in the C5H8 absorption.
The linelist covers 800-1870 cm^{-1} and 2700-3200 cm^{-1} with a gap from 1870 to 2700 cm^{-1}

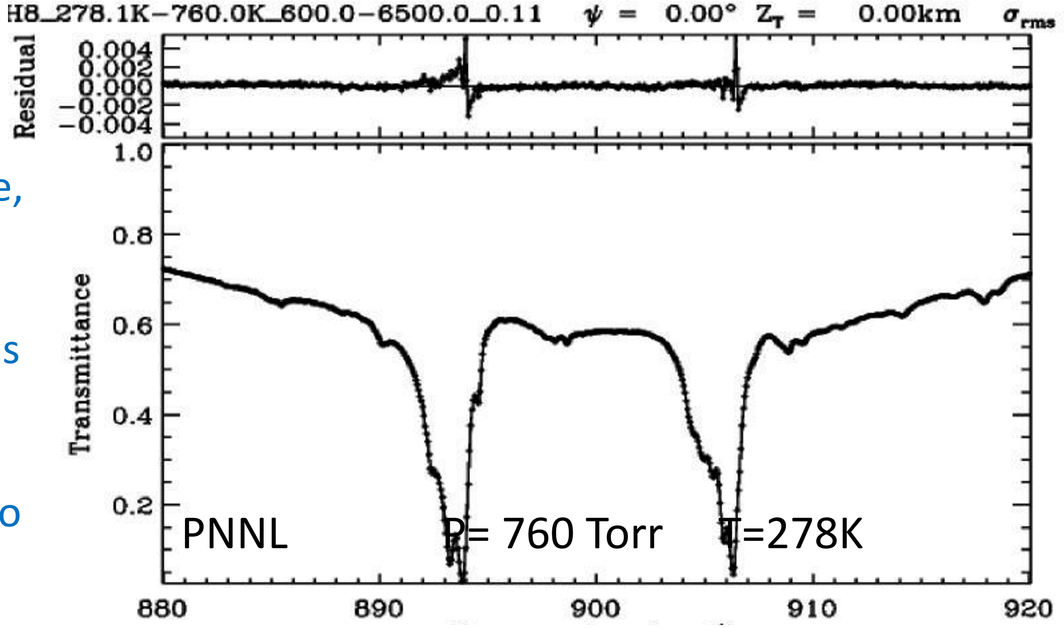
```
Center    Width MIT A I F  Parameters to fit   Gases fitted
 876.50 153.00  10 1 1 0  ncbf=0   xs   xo   xf   : c5h8 h2o
 994.00  82.00  10 1 1 0  ncbf=0   xs   xo   xf   : c5h8 h2o
1075.00  80.00  10 1 1 0  ncbf=0   xs   xo   xf   : c5h8 h2o
1160.00  90.00  10 1 1 0  ncbf=0   xs   xo   xf   : c5h8 h2o
1272.00 134.00  10 1 1 0  ncbf=0   xs   xo   xf   : c5h8 h2o
1419.50 161.00  10 1 1 0  ncbf=0   xs   xo   xf   : c5h8 h2o
1527.50  55.00  10 1 1 0  ncbf=0   xs   xo   xf   : c5h8 h2o
1626.00 142.00  10 1 1 0  ncbf=0   xs   xo   xf   : c5h8 h2o
1783.50 173.00  10 1 1 0  ncbf=0   xs   xo   xf   : c5h8 h2o

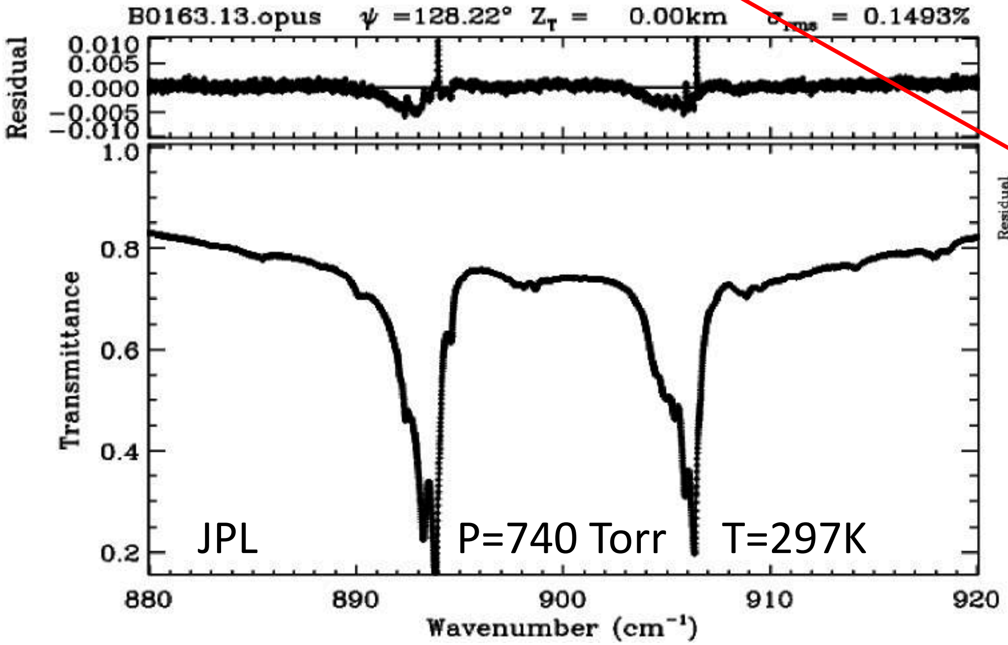
2950.00 500.00  10 1 1 0  ncbf=0   xs   xo   xf   : c5h8 h2o
```

Examples of Spectral Fits

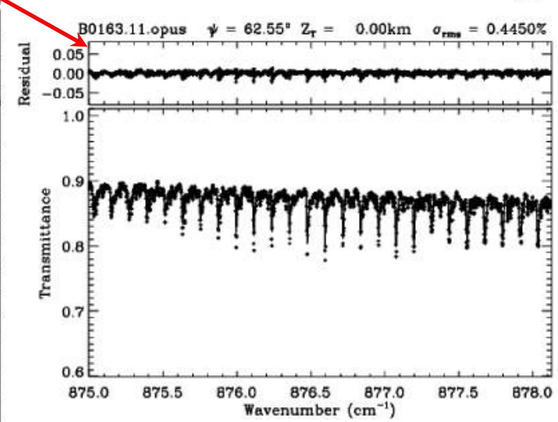


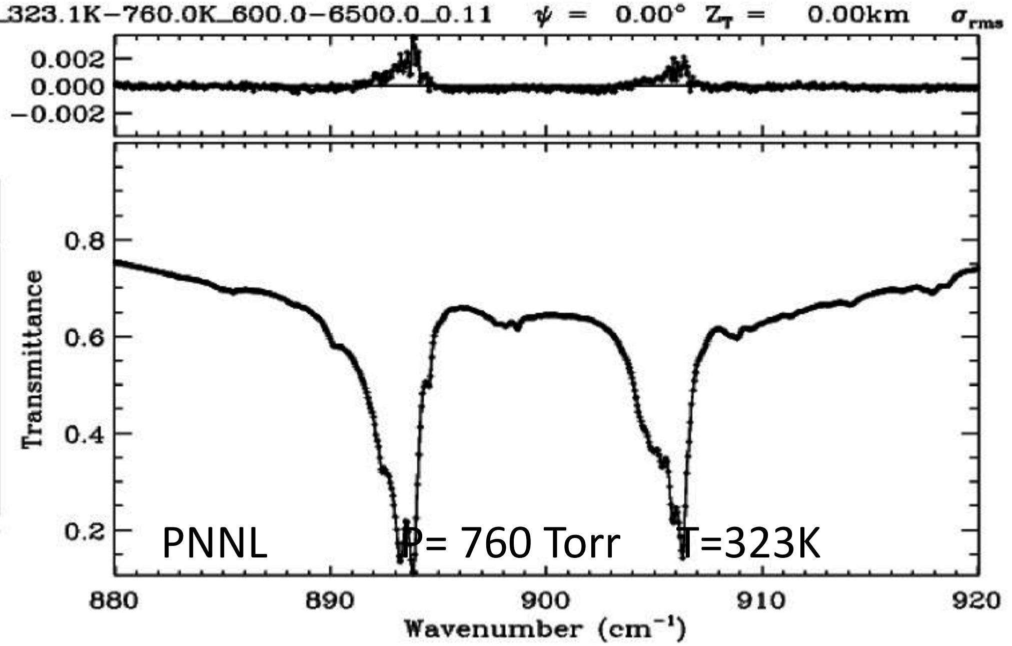
Although the low-Pressure, JPL spectrum (upper-left) look noisy, much of the structure in the residuals is actually spectral lines not fully captured by the EPLL because it is not needed to fit the high-P spectra.





Inset below shows portion of the JPL low-P spectrum.



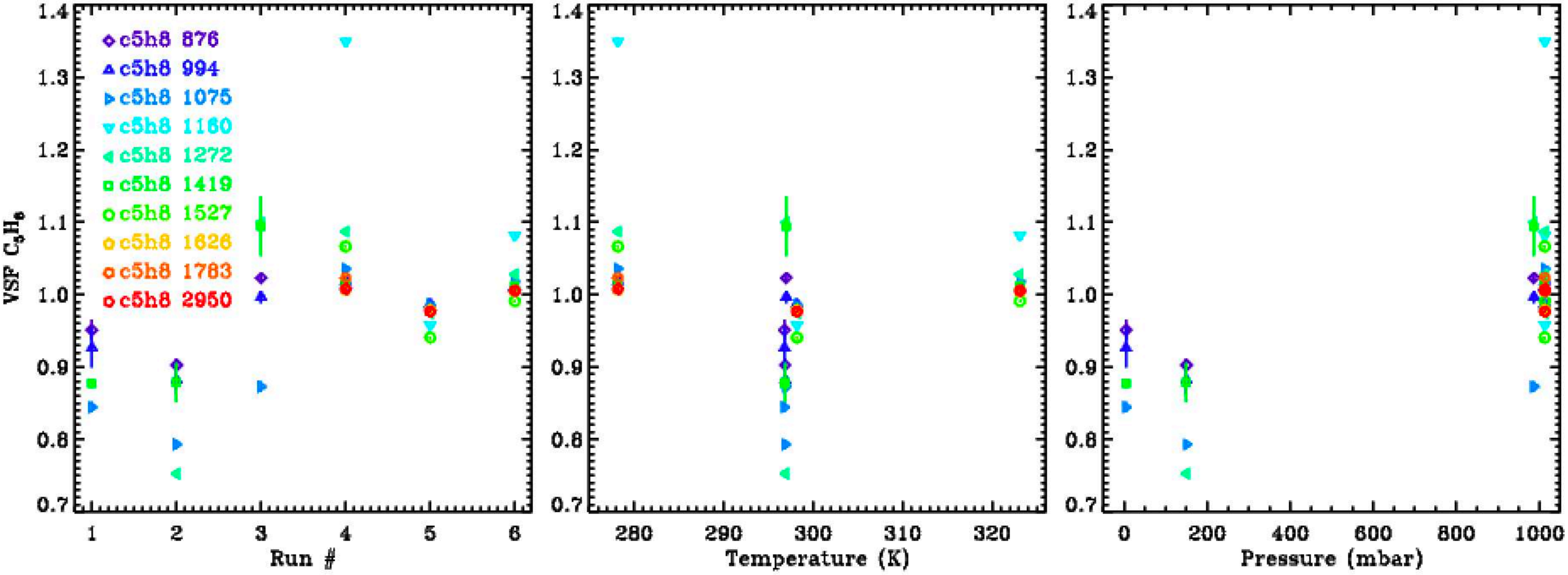


Retrieved C_5H_8 VMR Scale Factors (VSFs)

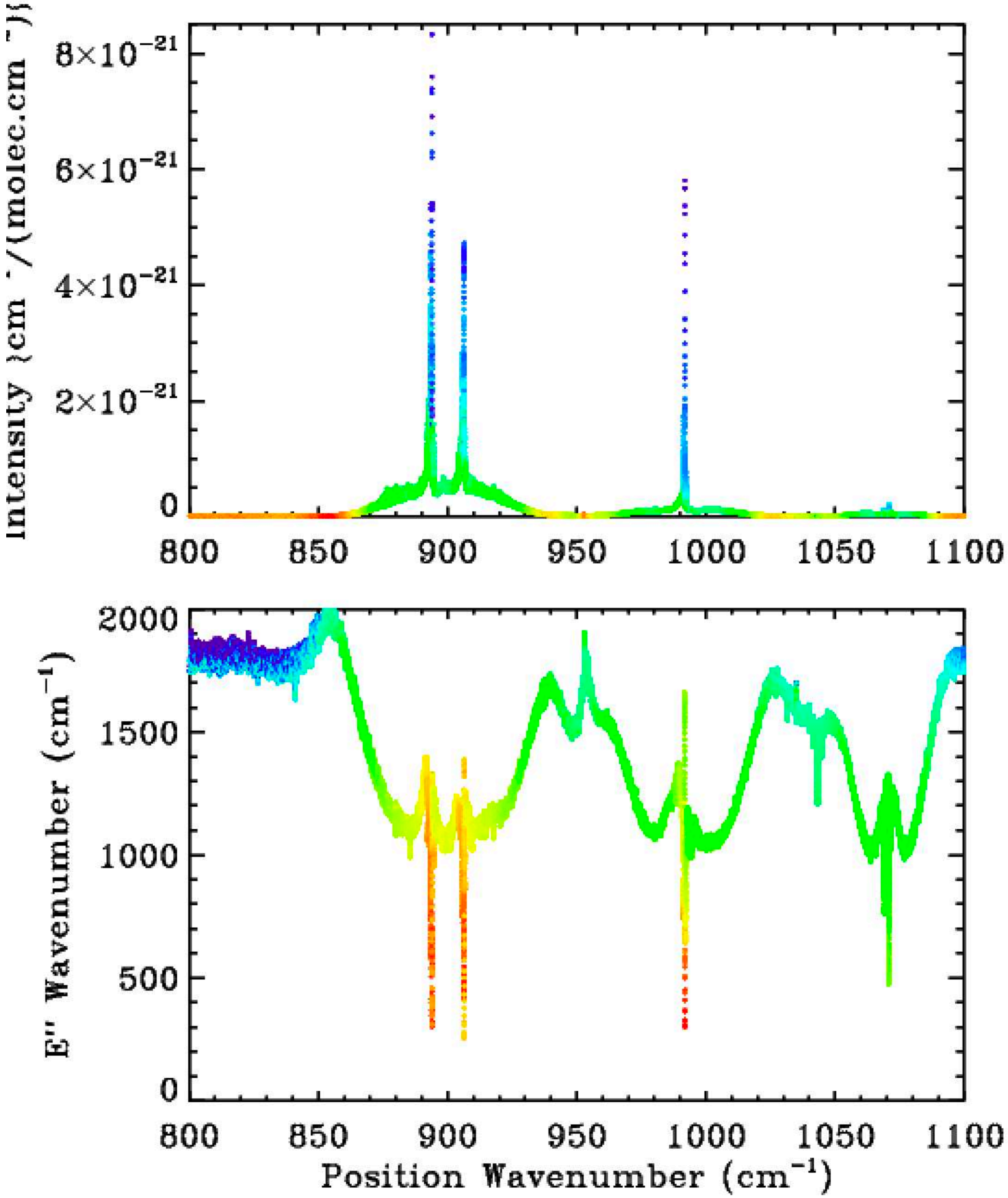
Runs 1-3 are the JPL spectra, which only cover the first 6 windows. Runs 4-6 are PNNL and cover all 10 windows.

The window centered at 1160 cm^{-1} has very weak absorption and hence erroneous VSF values.

The lower pressure spectra (JPL) tend to produce C_5H_8 amounts that are ~10% lower than those at 1 atm.

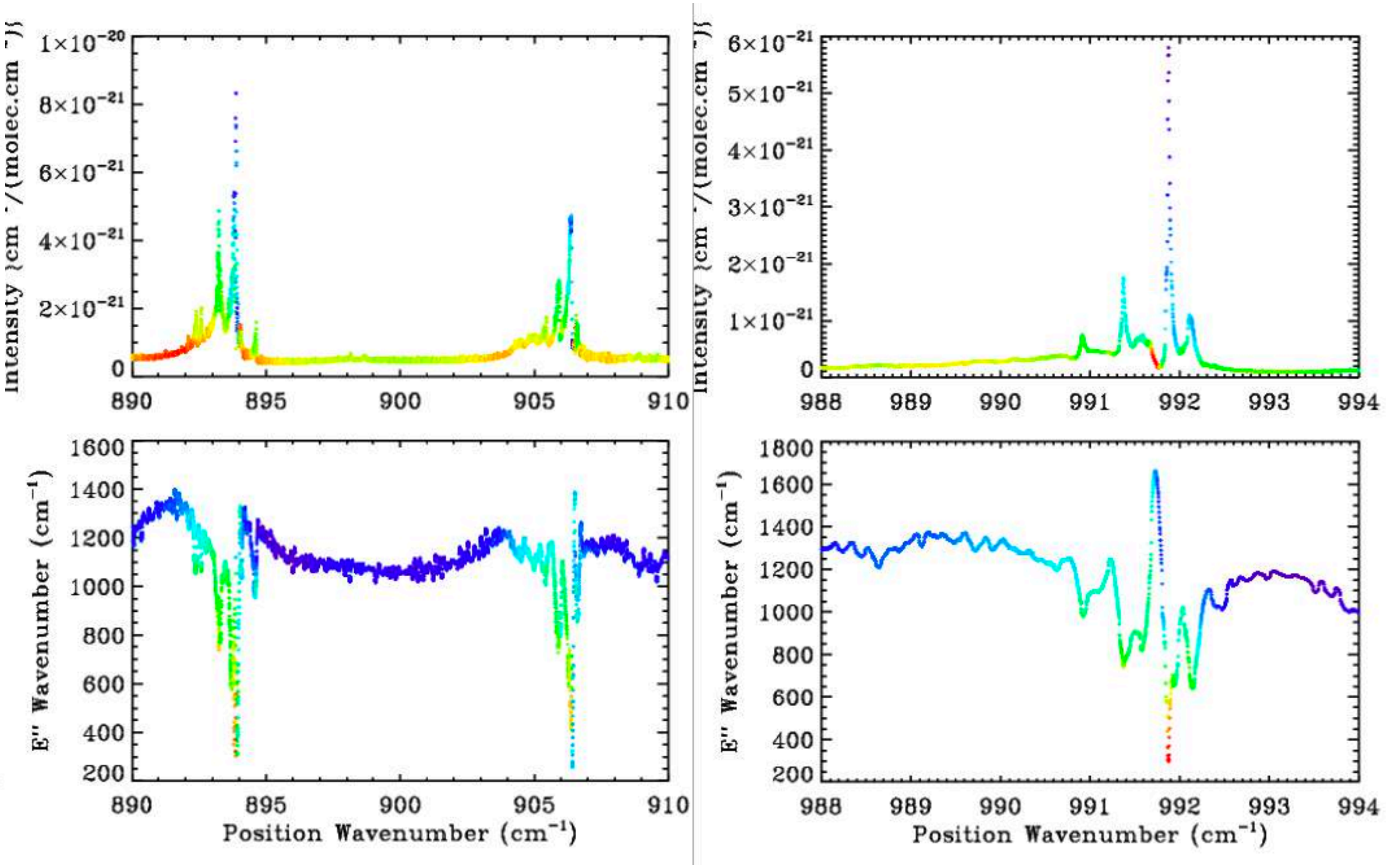


Derived Pseudo-Line Intensities and E” (1/3)

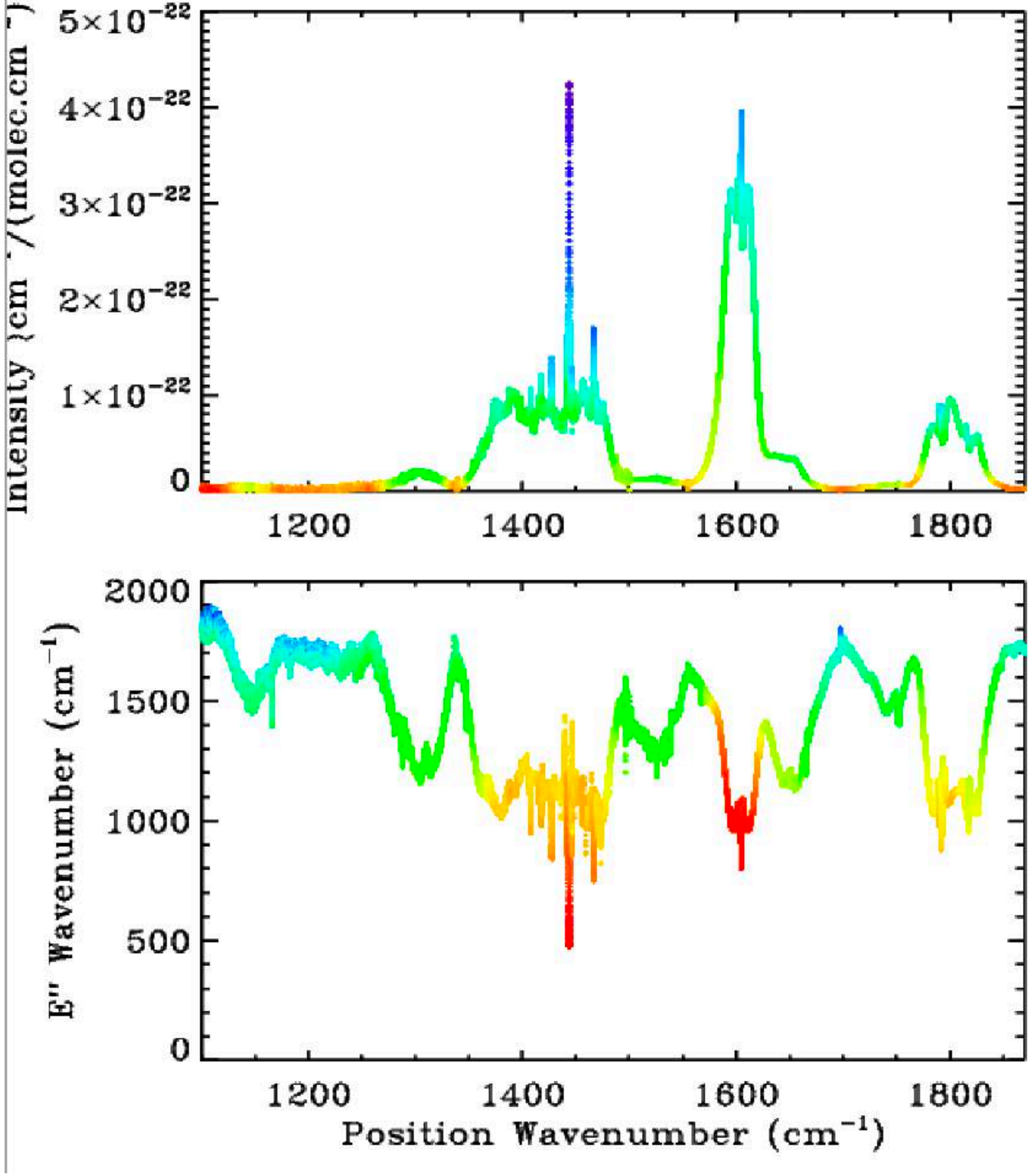


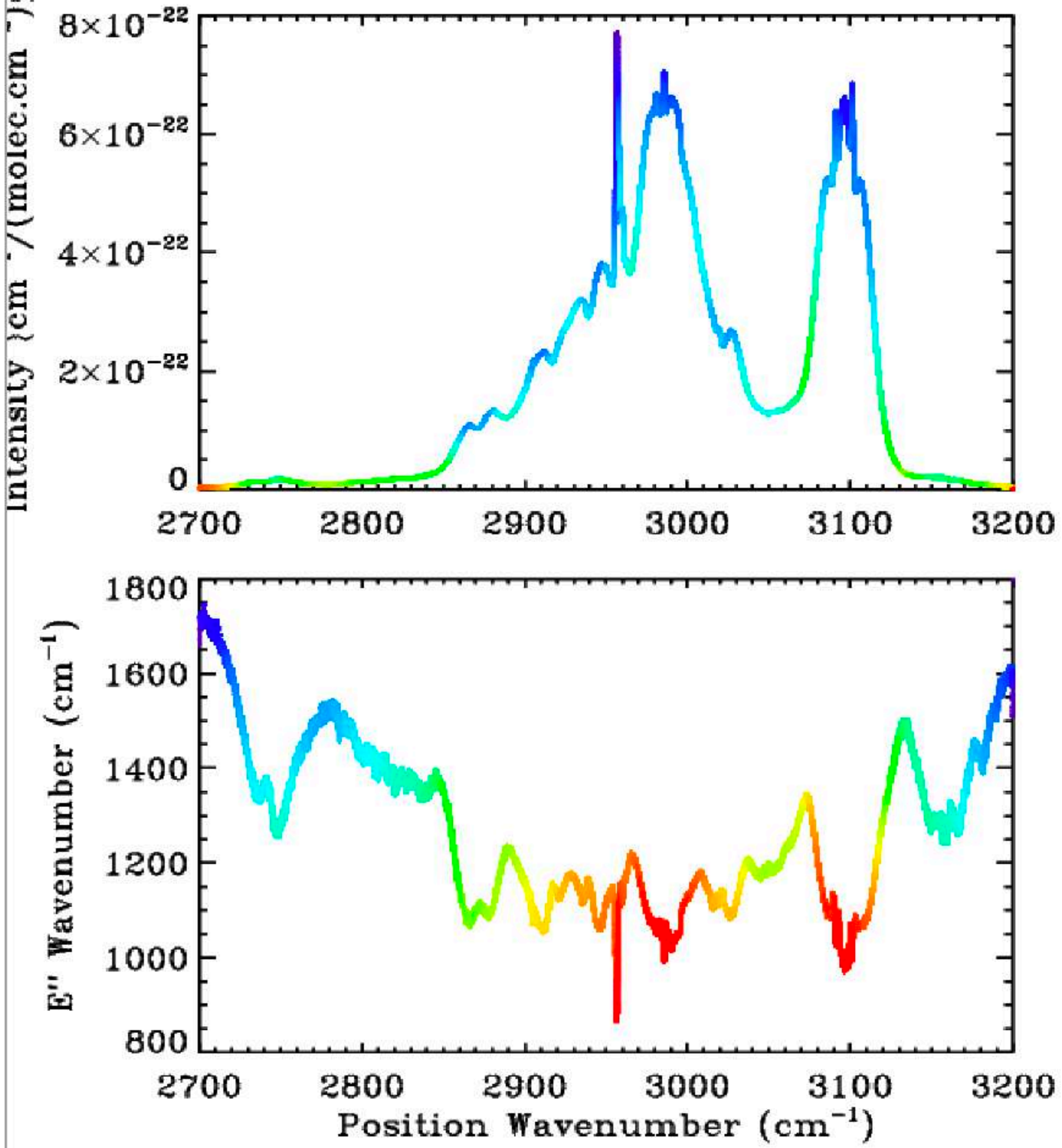
Left: Upper panel shows intensities color-coded by E” (blue=low; red=high). Lower panel shows E” color-coded by Intensity.

Below: Zoom into the sharp Q-branches at 894, 906, and 992 cm^{-1}.

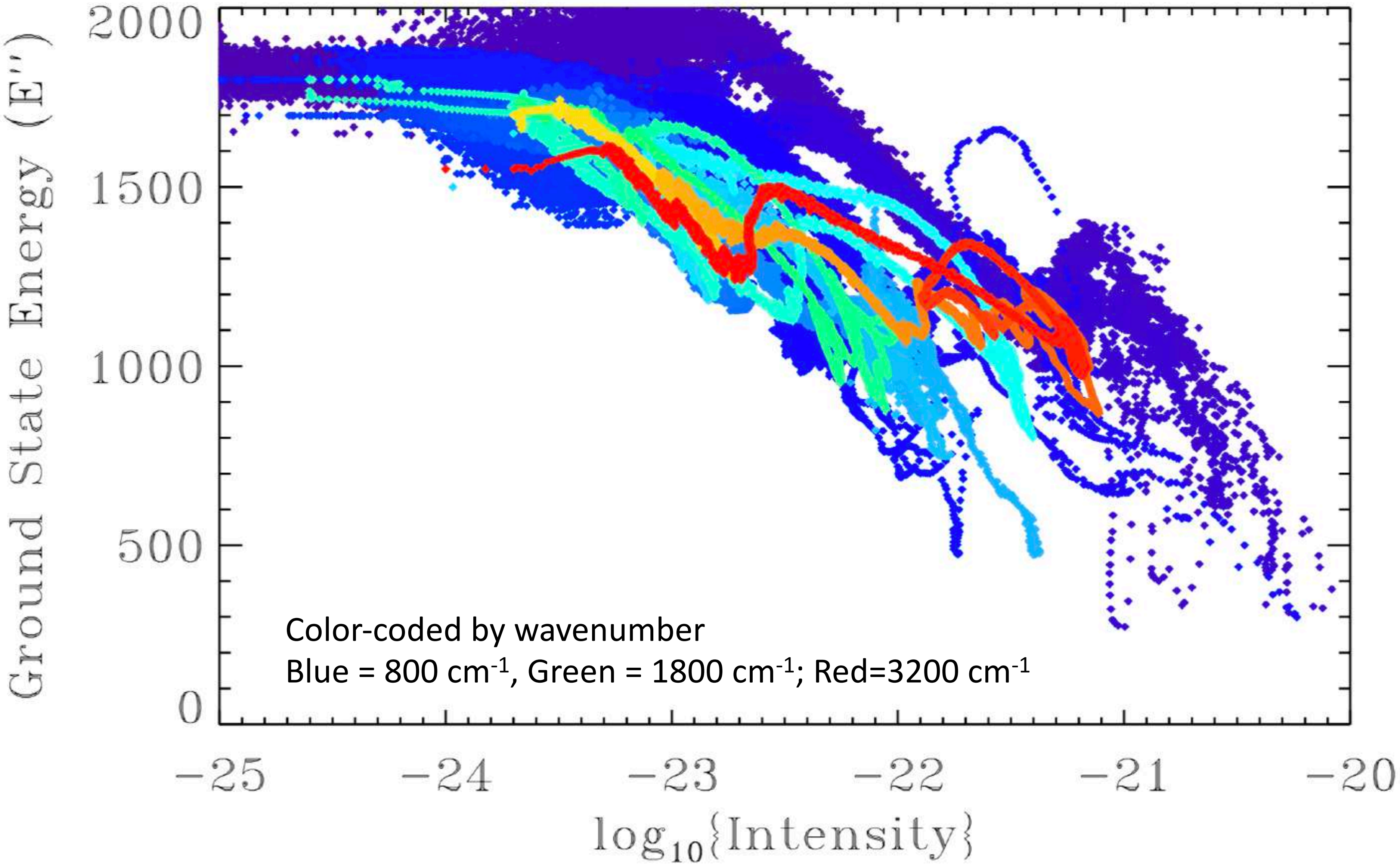


Derived Pseudo-Line Intensities and E” (2/3)





Derived Pseudo-Line Intensities and E” (3/3)



Color-coded by wavenumber
Blue = 800 cm^{-1}, Green = 1800 cm^{-1}; Red=3200 cm^{-1}

Comparison of wavenumber-integrated Intensities

Brauer et al., (2014)

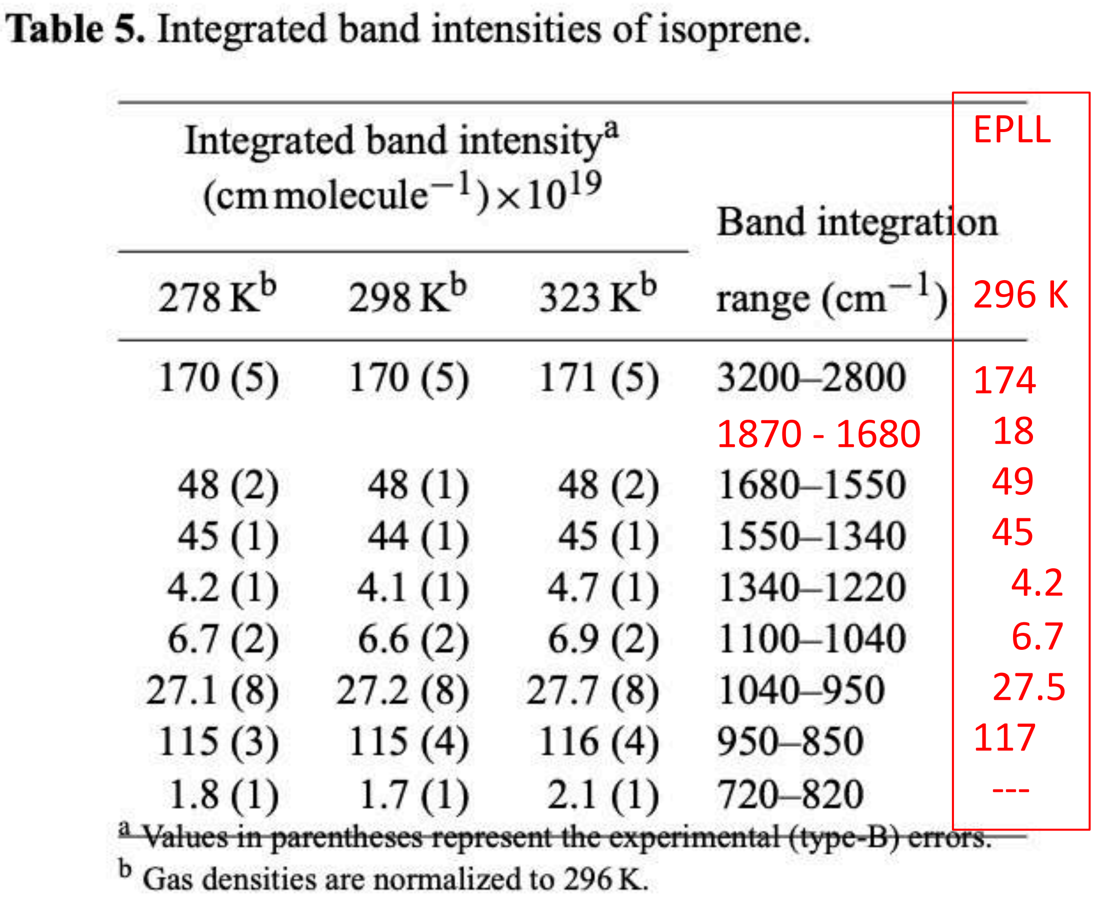


Table 5. Integrated band intensities of isoprene.

Integrated band intensity[a] (cm molecule^{-1})×10^{19} 278 K[b]	298 K[b]	323 K[b]	Band integration range (cm^{-1})	EPLL 296 K
170 (5)	170 (5)	171 (5)	3200–2800	174
			1870 - 1680	18
48 (2)	48 (1)	48 (2)	1680–1550	49
45 (1)	44 (1)	45 (1)	1550–1340	45
4.2 (1)	4.1 (1)	4.7 (1)	1340–1220	4.2
6.7 (2)	6.6 (2)	6.9 (2)	1100–1040	6.7
27.1 (8)	27.2 (8)	27.7 (8)	1040–950	27.5
115 (3)	115 (4)	116 (4)	950–850	117
1.8 (1)	1.7 (1)	2.1 (1)	720–820	---

[a] Values in parentheses represent the experimental (type-B) errors.
[b] Gas densities are normalized to 296 K.

Good consistency between Brauer et al. (2014) values and the 296K EPLL (obtained by summing the pseudo-line intensities).

For the regions above 1550 cm^{-1}, the JPL has no contribution whatsoever to the EPLL, so the excellent agreement is to be expected there. But at the lower wavenumbers, the level of agreement is surprising, given the ~10% discrepancy in the low-pressure JPL measurements.

Perhaps the JPL data were mostly ignored due to their larger fitting residuals?

Strange that Brauer at al. include the extremely weak 720-820 cm^{-1} region (100 times weaker than 2800-3200 cm^{-1}) in their table, but not the 1680-1870 cm^{-1} region which is 10x stronger.

Summary & Conclusions

A HITRAN-format empirical pseudo-line-list (EPLL) has been generated for isoprene from two sets of lab spectra:

- PNNL (Brauer et al. 2014) cover 600-6000 cm^{-1} at temperatures of 278K, 298K, and 323 K, but all at 760 Torr
- JPL (Keeyoon Sung) cover 550-1550 cm^{-1} at pressures of 4, 112, and 740 Torr, but all at 297K

The low-pressure JPL data expose higher resolution structure, e.g. in the strong Q-branches at 896, 904 and 992 cm^{-1}, which may be important for analyzing lower-pressure open-path atmospheric spectra.

The temperature-variation of the PNNL data allow the derivation of ground-state energies, which average 1000 cm^{-1} because isoprene has several low-lying vibrational modes which become strongly populated at 296K, driving up the E”.

The results between these two datasets seem consistent to within 5% at 297K and 1 atm.

The resulting PLL covers:

- 800 to 1870 cm^{-1} with 0.1 cm^{-1} margins at a line spacing of 0.0025 cm^{-1} (428,081 lines)
- 2700 to 3200 cm^{-1} with 0.1 cm^{-1} margins at a line spacing of 0.0050 cm^{-1} (100,041 lines)

The isoprene amounts retrieved from the lab spectra are generally consistent to within 10% of the expected amounts.

If significant quantities of atmospheric isoprene exist at temperatures below 278K, additional lab spectra are needed.

The isoprene EPLL is available from: https://mark4sun.jpl.nasa.gov/pseudo.html