Acetone Empirical Pseudo-Line-List

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An empirical pseudo-linelist (PLL) has been derived from lab cross-sections. The PLL covers 700-1910 and 2615-3250 cm^{-1} at a line spacing of 0.005 cm^{-1}, giving a total of 305,502 lines.

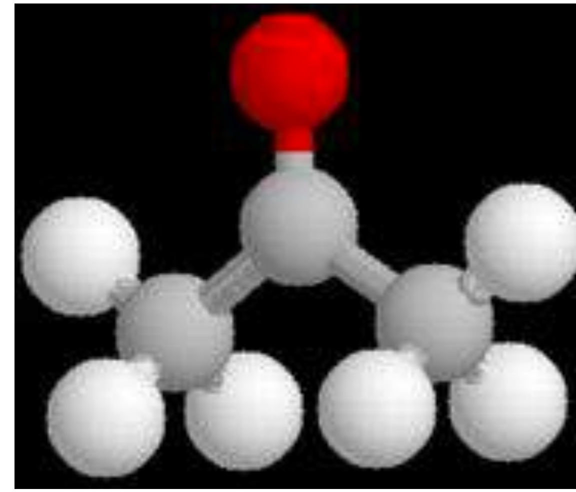
This PLL can be downloaded from:
mark4sun.jpl.nasa.gov/pseudolines/data/CH3COCH3.101.gz

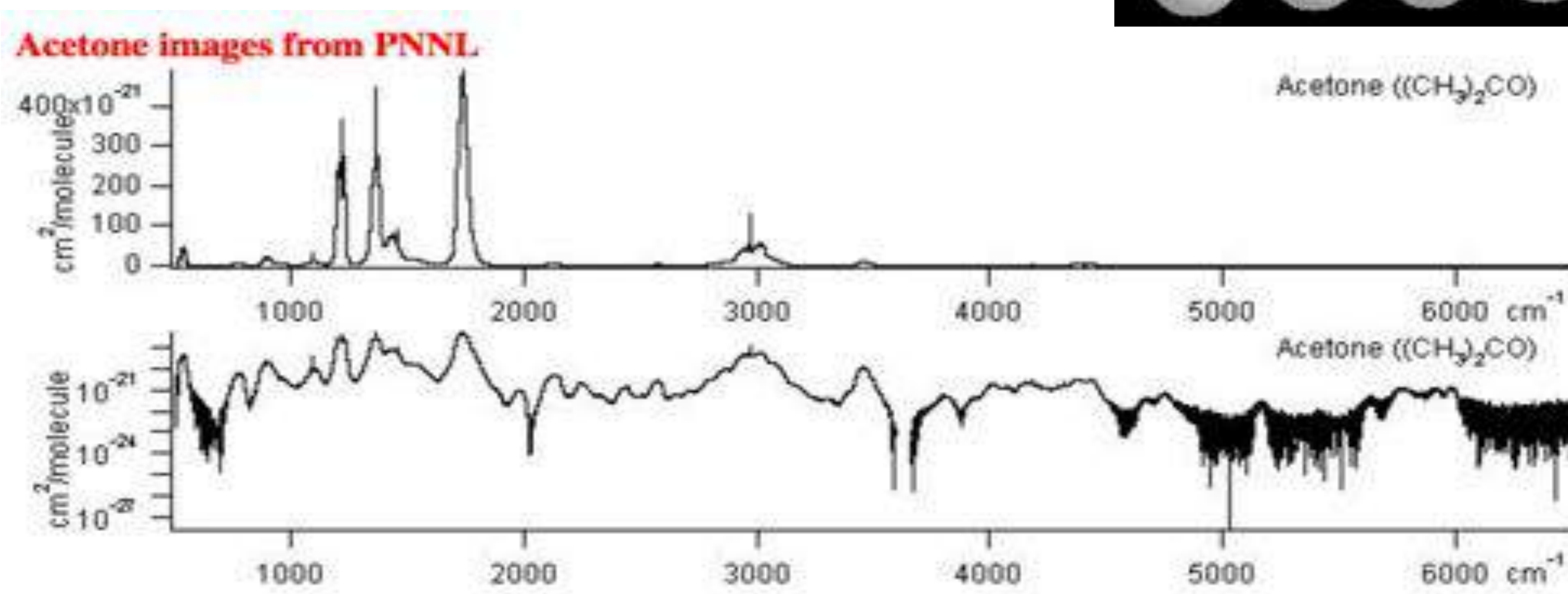
Acetone Absorption Spectrum (PNNL)

Strongest band is the v_3 (C-O stretch) at 1730 cm^{-1} which is unfortunately blacked out from the Earth's surface.

So are the two overlapping v_5 and v_{16} bands (CH_3 deform) centered at 1364 cm^{-1} – the second-strongest band.

For Earth ground-based remote sensing, the best bands are the v_{17} (C-C stretch) at 1216 cm^{-1} and the five overlapping C-H stretch bands at 2930-3020 cm^{-1}.





Access to lab cross-section data

Cross-sections were downloaded from:
http://hitran.org/suppl/xsec/HITRAN2012/CH3COCH3_IR11_alt.zip
This is the supplementary directory where the original cross-sections of Harrison and Waterfall are preserved (without setting negative values to zero).

These represent the work of Harrison et al., (2011a,b) the latter paper describing unpublished data of Waterfall et al.

Also used the PNNL cross-sections downloaded from: https://secure2.pnl.gov/nsd/nsd.nsf

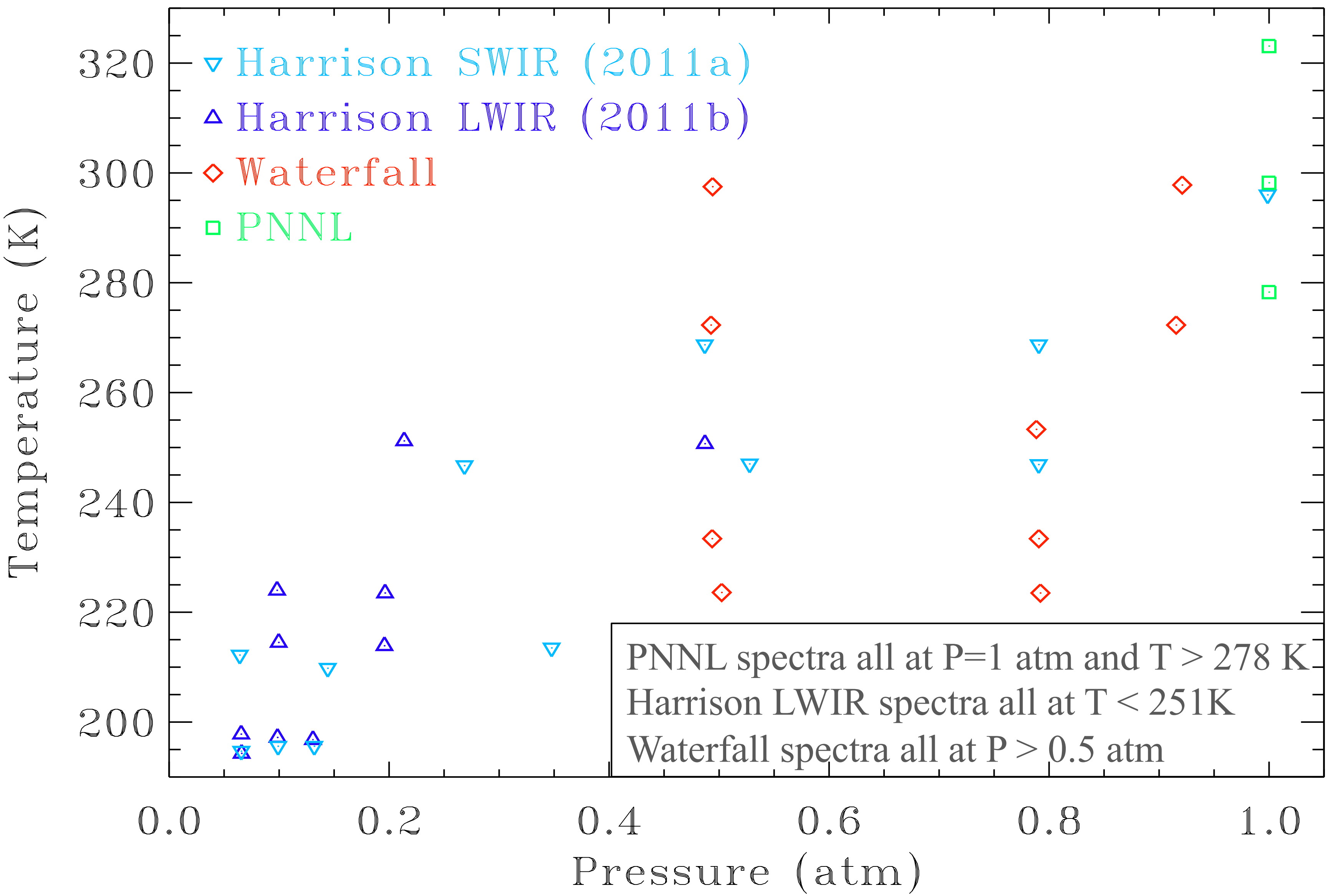
Harrison, Jeremy & D.C. Allen, Nicholas & F. Bernath, Peter. (2011a). Infrared absorption cross sections for acetone (propanone) in the 3µm region. Journal of Quantitative Spectroscopy and Radiative Transfer, 112, 53-58.

Harrison, J.J., Humpage, N., Allen, N.D., Waterfall, A.M., Bernath, P.F. and Remedios, J.J., (2011b). Mid-infrared absorption cross sections for acetone (propanone). Journal of Quantitative Spectroscopy and Radiative Transfer, 112, 457-464

List of Analyzed Lab Spectra

File Name	Nu1	Nu2	Npts	Temp	Pres	PP	Length	Res	Comment
Acetone_LWIR_194.3K_050.15Torr	830	1950	223020	194.3	50.1	0.020	17.7	.015	Harrison (2011b)
Acetone_LWIR_196.8K_099.38Torr	830	1950	223021	196.8	99.4	0.041	17.7	.015	Harrison (2011b)
Acetone_LWIR_197.2K_074.92Torr	830	1950	223024	197.2	74.9	0.041	17.7	.015	Harrison (2011b)
Acetone_LWIR_197.8K_049.79Torr	830	1950	223024	197.8	49.8	0.041	17.7	.015	Harrison (2011b)
Acetone_LWIR_213.9K_148.75Torr	830	1950	223021	213.9	148.8	0.100	6.5	.015	Harrison (2011b)
Acetone_LWIR_214.5K_075.69Torr	830	1950	223021	214.5	75.7	0.100	6.5	.015	Harrison (2011b)
Acetone_LWIR_223.5K_149.25Torr	830	1950	223019	223.5	149.2	0.090	6.5	.015	Harrison (2011b)
Acetone_LWIR_224.0K_074.61Torr	830	1950	223018	224.0	74.6	0.093	6.5	.015	Harrison (2011b)
Acetone_LWIR_250.7K_370.22Torr	830	1950	223018	250.7	370.2	0.615	1.7	.015	Harrison (2011b)
Acetone_LWIR_251.2K_162.40Torr	830	1950	223018	251.2	162.4	0.622	1.7	.015	Harrison (2011b)
acetone_WF_223.5K_602.0Torr	700	1780	71685	223.5	602.0	0.100	10.0	.032	Waterfall
acetone_WF_223.6K_381.8Torr	700	1780	71685	223.6	381.8	0.100	10.0	.032	Waterfall
acetone_WF_233.4K_375.2Torr	700	1780	71685	233.4	375.2	0.100	10.0	.032	Waterfall
acetone_WF_233.4K_600.9Torr	700	1780	71685	233.4	600.9	0.100	10.0	.032	Waterfall
acetone_WF_253.3K_599.2Torr	700	1780	71685	253.3	599.2	0.100	10.0	.032	Waterfall
acetone_WF_272.3K_374.4Torr	700	1780	71685	272.3	374.4	0.100	10.0	.032	Waterfall
acetone_WF_272.3K_695.8Torr	700	1780	71685	272.3	695.8	0.100	10.0	.032	Waterfall
acetone_WF_297.5K_375.5Torr	700	1780	71685	297.5	375.5	0.100	10.0	.032	Waterfall
acetone_WF_297.8K_700.0Torr	700	1780	71685	297.8	700.0	0.100	10.0	.032	Waterfall
Acetone_SWIR_194.7K_49.92Torr	2615	3300	136400	194.7	49.9	0.053	19.3	.015	Harrison (2011a)
Acetone_SWIR_195.6K_75.34Torr	2615	3300	136400	195.6	75.3	0.058	19.3	.015	Harrison (2011a)
Acetone_SWIR_195.6K_100.33Torr	2615	3300	136400	195.6	100.3	0.058	19.3	.015	Harrison (2011a)
Acetone_SWIR_209.8K_109.63Torr	2615	3300	136400	209.8	109.6	0.126	19.3	.015	Harrison (2011a)
Acetone_SWIR_212.2K_48.82Torr	2615	3300	136400	212.2	48.8	0.143	19.3	.015	Harrison (2011a)
Acetone_SWIR_213.5K_264.29Torr	2615	3300	136400	213.5	264.3	0.112	19.3	.015	Harrison (2011a)
Acetone_SWIR_246.7K_204.1Torr	2615	3300	136400	246.7	204.1	0.413	8.1	.015	Harrison (2011a)
Acetone_SWIR_246.9K_600.8Torr	2615	3300	136400	246.9	600.8	0.384	8.1	.015	Harrison (2011a)
Acetone_SWIR_247.0K_401.1Torr	2615	3300	136400	247.0	401.1	0.369	8.1	.015	Harrison (2011a)
Acetone_SWIR_268.7K_370.1Torr	2615	3300	136400	268.7	370.1	0.681	4.9	.015	Harrison (2011a)
Acetone_SWIR_268.7K_600.9Torr	2615	3300	136400	268.7	600.9	0.679	4.9	.015	Harrison (2011a)
Acetone_SWIR_296.0K_759.05Tor	2615	3300	136400	296.0	759.0	0.997	3.3	.015	Harrison (2011a)
ACETONE_5T.TXT	510	6500	100000	278.26	760	0.076	1.0	.10	PNNL
ACETONE_25T.TXT	510	6500	100000	298.16	760	0.076	1.0	.10	PNNL
ACETONE_50T.TXT	510	6500	100000	323.12	760	0.076	1.0	.10	PNNL

Lab Measurement Conditions



Partition Function

Assumed Harmonic Oscillator Approximation (HOA) with:

- Rotational PF: $(296/T)^{1.5}$
- Vibrational PF used the 24 modes listed below each with a degeneracy of 1

Fundamental frequencies from NIST Chemistr

n_1 3019 cm^{-1} (a_1) CH_3 d-stretch
n_2 2937 cm^{-1} (a_1) CH_3 s-stretch
n_3 1731 cm^{-1} (a_1) CO stretch
n_4 1435 cm^{-1} (a_1) CH_3 d-deform
n_5 1364 cm^{-1} (a_1) CH_3 s-deform
n_6 1066 cm^{-1} (a_1) CH_3 rock
n_7 777 cm^{-1} (a_1) CC stretch
n_8 385 cm^{-1} (a_1) CCC deform
n_9 2963 cm^{-1} (a_2) CH_3 d-stretch
n_{10} 1426 cm^{-1} (a_2) CH_3 d-deform
n_{11} 877 cm^{-1} (a_2) CH_3 rock
n_{12} 105 cm^{-1} (a_2) torsion

n_{13} 3019 cm^{-1} (b_1) CH_3 d-stretch
n_{14} 2937 cm^{-1} (b_1) CH_3 s-stretch
n_{15} 1410 cm^{-1} (b_1) CH_3 d-deform
n_{16} 1364 cm^{-1} (b_1) CH_3 s-deform
n_{17} 1216 cm^{-1} (b_1) CC stretch
n_{18} 891 cm^{-1} (b_1) CH_3 rock
n_{19} 530 cm^{-1} (b_1) CO in plane bend
n_{20} 2972 cm^{-1} (b_2) CH_3 d-stretch
n_{21} 1454 cm^{-1} (b_2) CH_3 d-deform
n_{22} 1091 cm^{-1} (b_2) CH_3 rock
n_{23} 484 cm^{-1} (b_2) CO out of plane bend
n_{24} 109 cm^{-1} (b_2) torsion

HOA is known to be poor in molecules with torsional modes, but provided users of the PLL make the same assumptions as were made in its generation, the error should mainly cancel.

Properties of Fitted Windows

Center	Width	MIT AIF	Fit Parameters	Smax	Stot	Sbar	E"bar	
765.2	129.6	10 1 1 0	xl xt xs xo cf	1.576E-22	3.826E-19	3.411E-23	710.6	W P
915.0	169.5	10 1 1 0	xl xt xs xo cf	2.805E-22	1.037E-18	6.041E-23	796.2	L W P
1075.0	150.0	10 1 1 0	xl xt xs xo cf	2.114E-22	6.514E-19	4.029E-23	759.8	L W P
1212.5	125.0	10 1 1 0	xl xt xs xo cf	1.904E-21	1.094E-17	1.060E-21	681.7	L W P
1452.5	355.0	10 1 1 0	xl xt xs xo cf	2.407E-21	1.721E-17	7.438E-22	626.4	L W P
1714.0	131.0	10 1 1 0	cl xt xs xo cf	2.656E-21	2.185E-17	1.648E-21	621.7	L W P
1772.5	285.0	10 1 1 0	cl xt xs xo xf	2.656E-21	2.342E-17	1.550E-21	620.5	L P
2932.7	634.9	10 1 1 0	xl xt xs xo xf	1.303E-21	7.533E-18	3.413E-22	613.6	S P

S means window is fully covered by the Harrison SWIR spectra: 2615 – 3300 cm^{-1}

W means window is fully covered by the Waterfall spectra: 700 – 1780 cm^{-1}

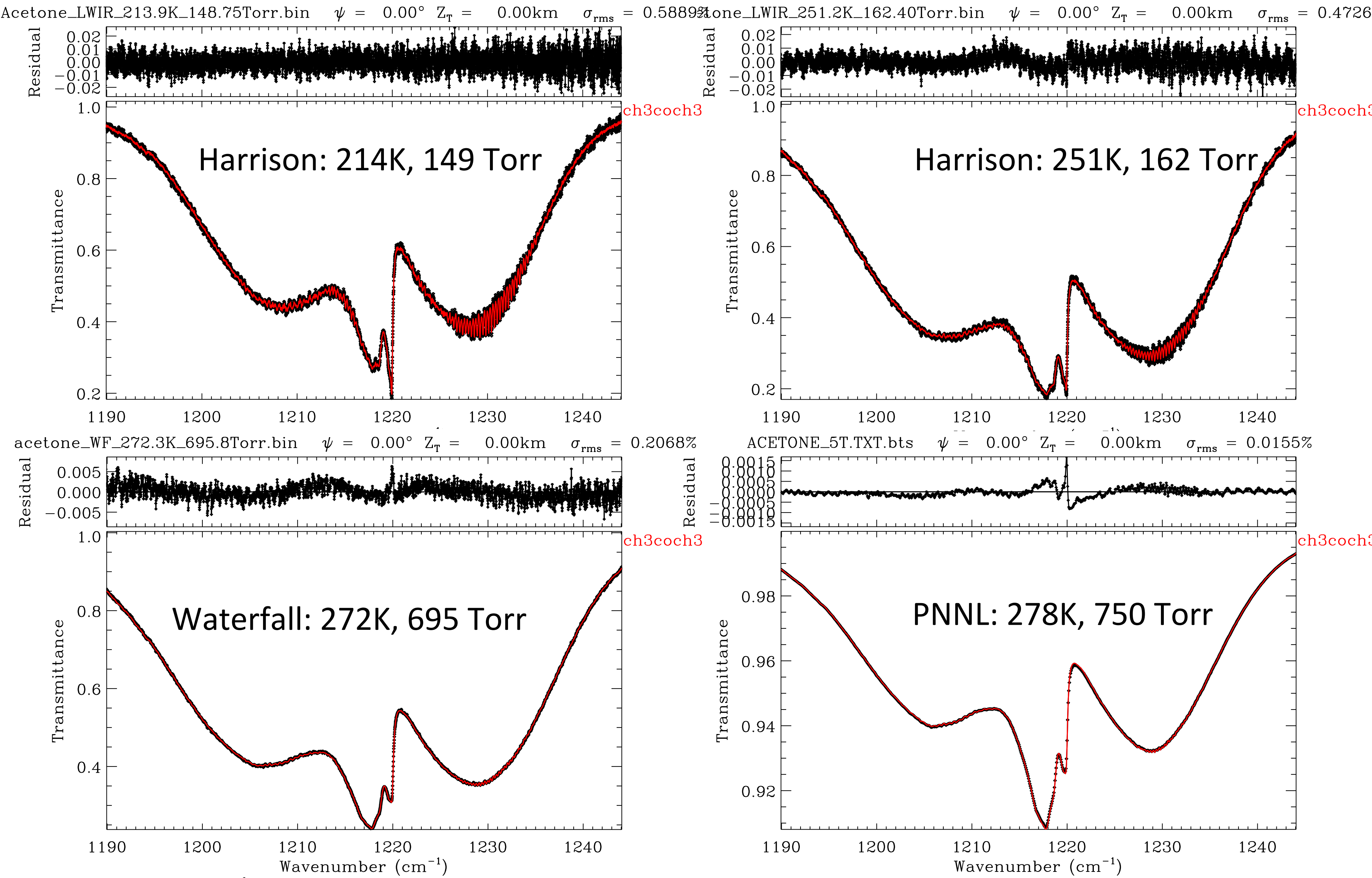
L means window is fully covered by the Harrison LWIR spectra : 830 – 1950 cm^{-1}

P means window is fully covered by the PNNL spectra: 510 – 6500 cm^{-1}

The 1714 cm^{-1} window is a subset of the 1772 cm^{-1} window. It is fitted separately because the Waterfall spectra, which end at 1780 cm^{-1}, don't cover the whole of the v_3 band. This risks creating a discontinuity in the PLL at 1780 cm^{-1} if there is any inconsistency between the Harrison LWIR and Waterfall cross-sections in this region

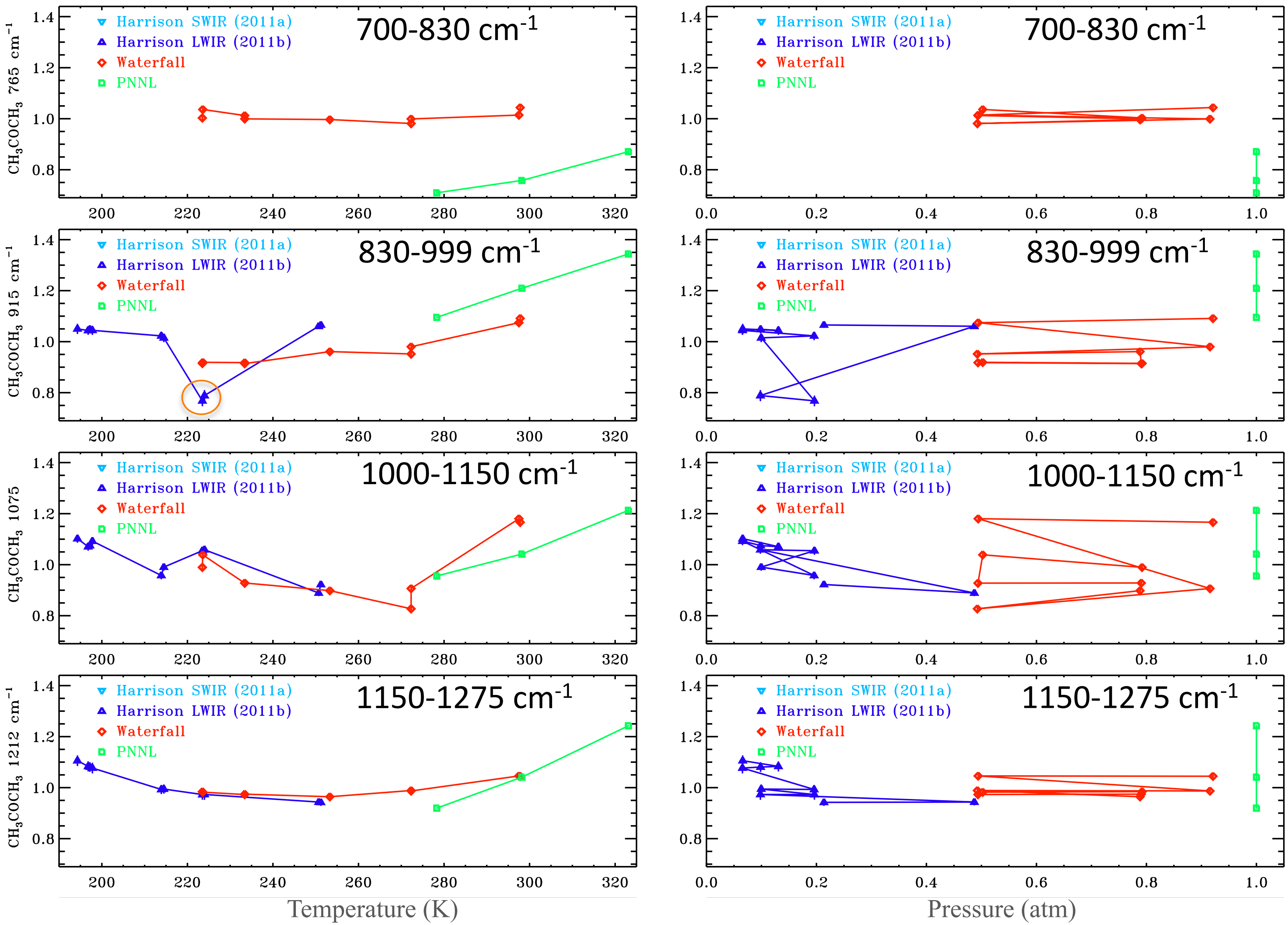
Harrison et al. removed channel fringes from their spectra, but Waterfall apparently did not. So for the windows covered by the Waterfall spectra, channel fringes ("cf") were fitted.

Examples of Spectral Fits around 1200 cm^{-1}



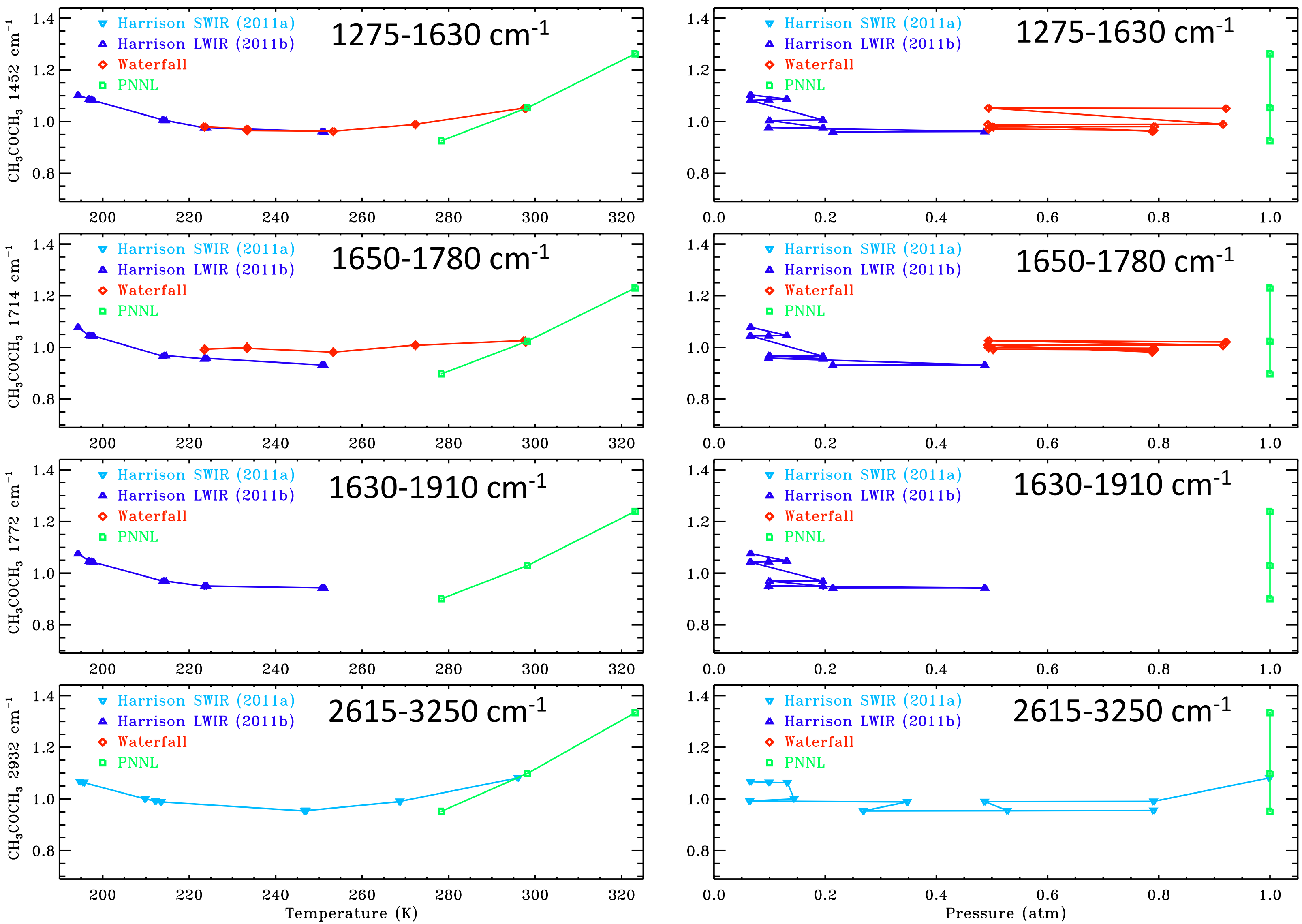
The 1200 cm^{-1} window is the one most likely to be useful for ground-based observations.

Retrieved VSFs: Windows 1-5



The VSFs are the factors by which the gas vmr was scaled to achieve best fit. Should all be 1.00.

Retrieved VSFs: Windows 5-8



Left panels show VSF versus temperature. Right panels show same VSFs versus pressure.

Retrieved gas amounts (VSF)

In terms of VSF versus Temperature

- Good agreement between Waterfall and PNNL at 296K
- Good agreement between Harrison SWIR and PNNL at 296K
- No overlap between Harrison LWIR and PNNL

Most windows show a shallow minimum in VSF at ~250K with values of ~ 0.95.

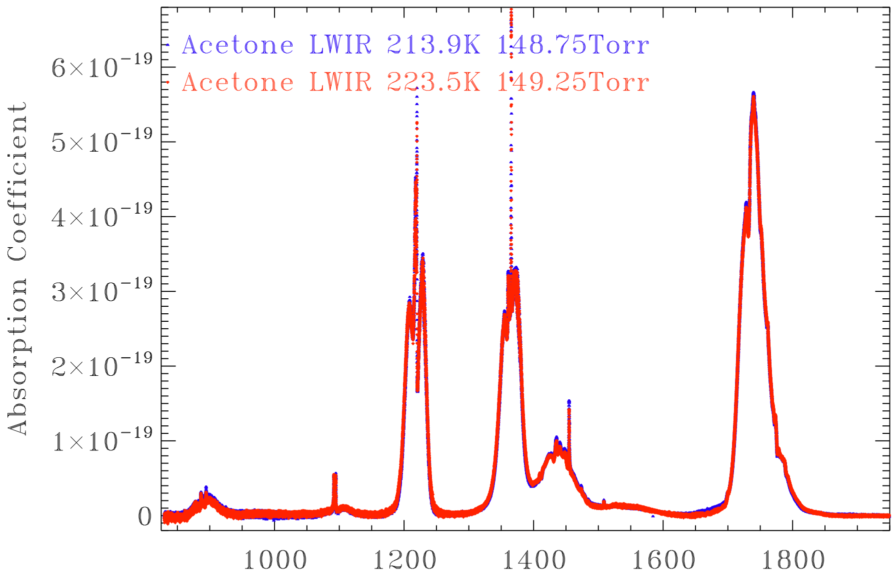
25-30% bias between Waterfall and PNNL at 700-830 cm^{-1} , but agreement in all other bands.

Harrison LWIR spectra measured at 224K are biased 25% low in 830-999 cm^{-1} window with respect to the other Harrison LWIR spectra. See yellow-circled points on previous slide. This appears to be due to negative cross-sections below 860 cm^{-1}.

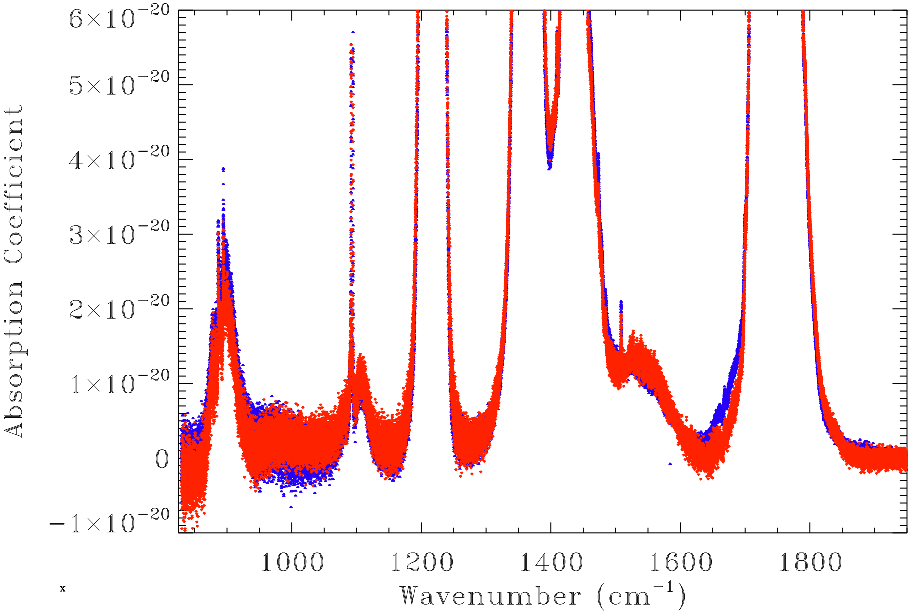
Strongly increasing VSF with Temperature for PNNL spectra in most windows.

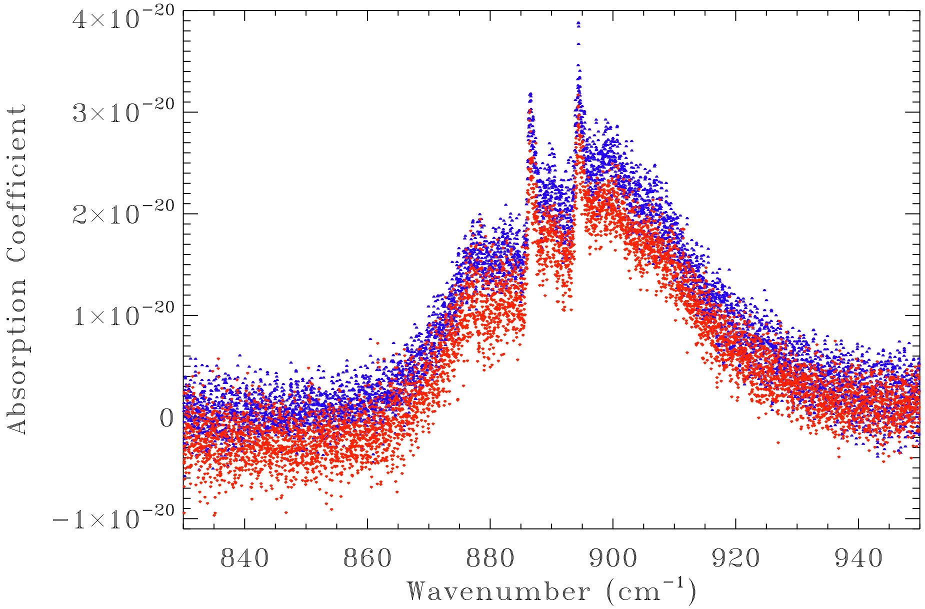
Significant positive curvature in all windows, except 700-830 cm^{-1} where it is negative. Positive curvature means that the effective E” increases with temperature. But since we force it to a constant value, this results in a dip in the VSFs plotted as a function of T.

Comparing Harrison 214K and 224K x-secs

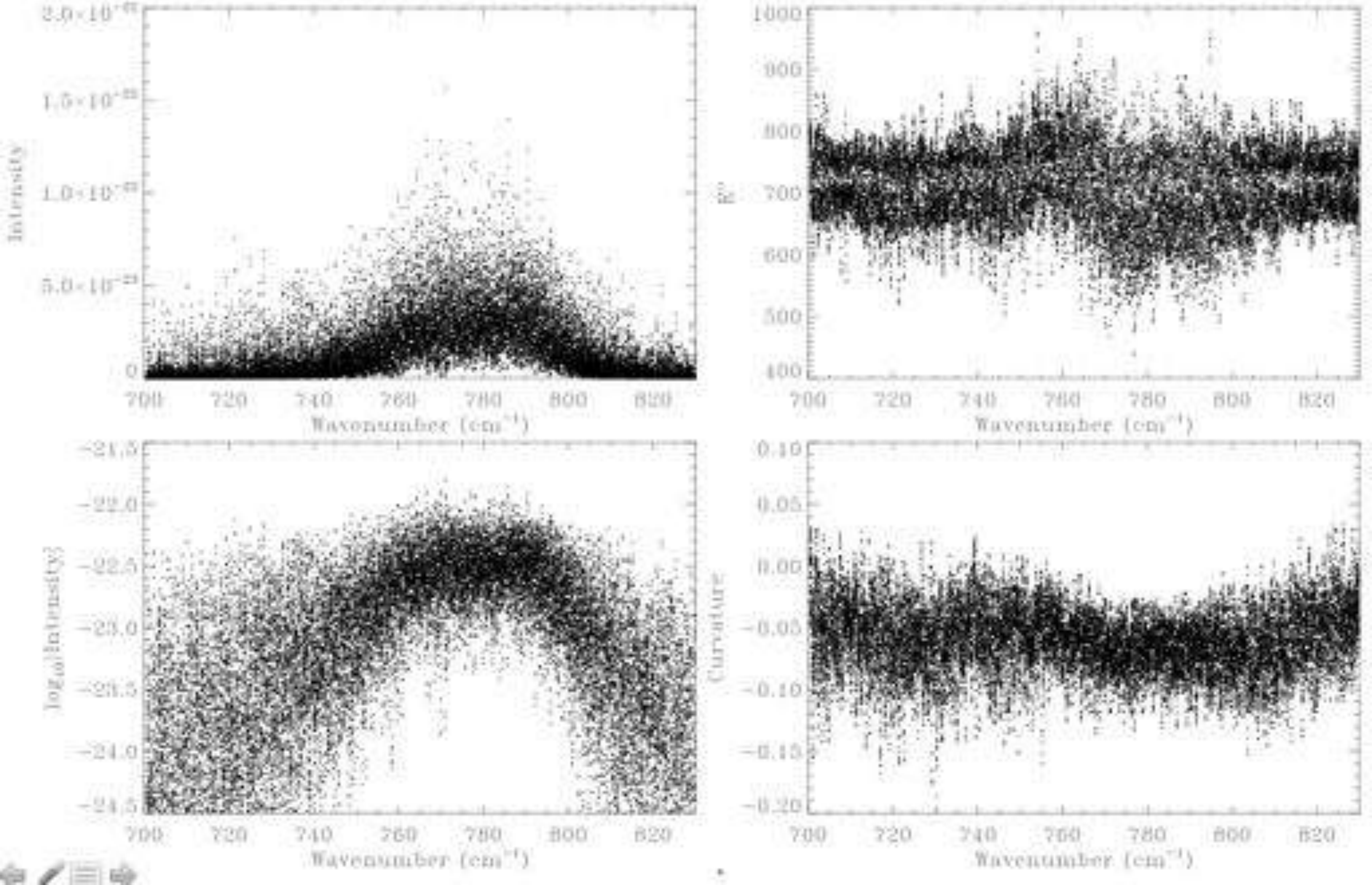


The Harrison 2011b 223.5K and 74.6 Torr absorption coefficients (red) become mainly negative below 850 cm^{-1}. This causes a 25% low gas amount (VSF) to be retrieved for this spectrum using this band. The spectrum at 224 K and 74.61Torr (not shown) has the same problem.
[Cross-sections smoothed by 4-point-wide triangle to reduce noise and figure file size]

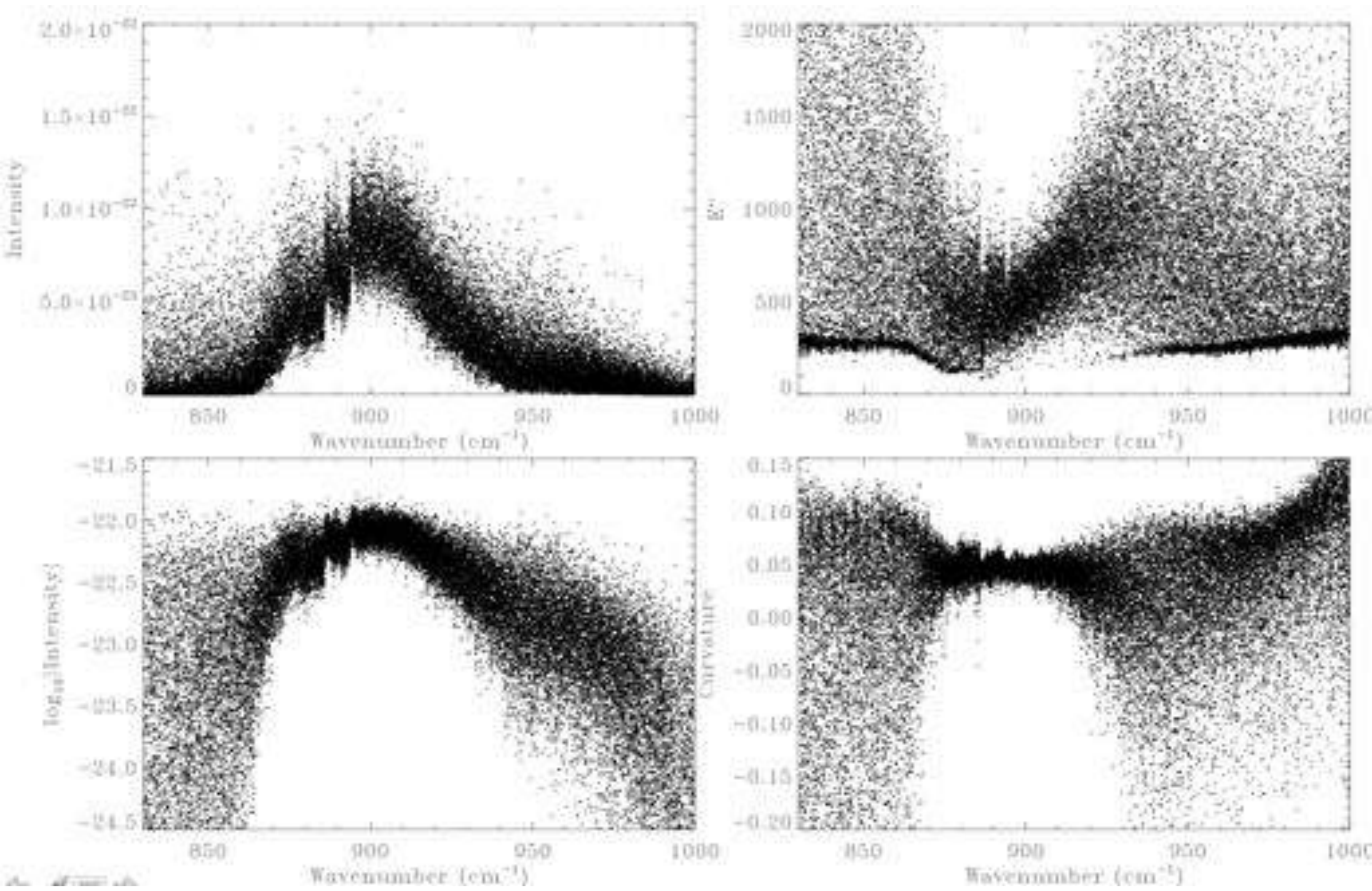




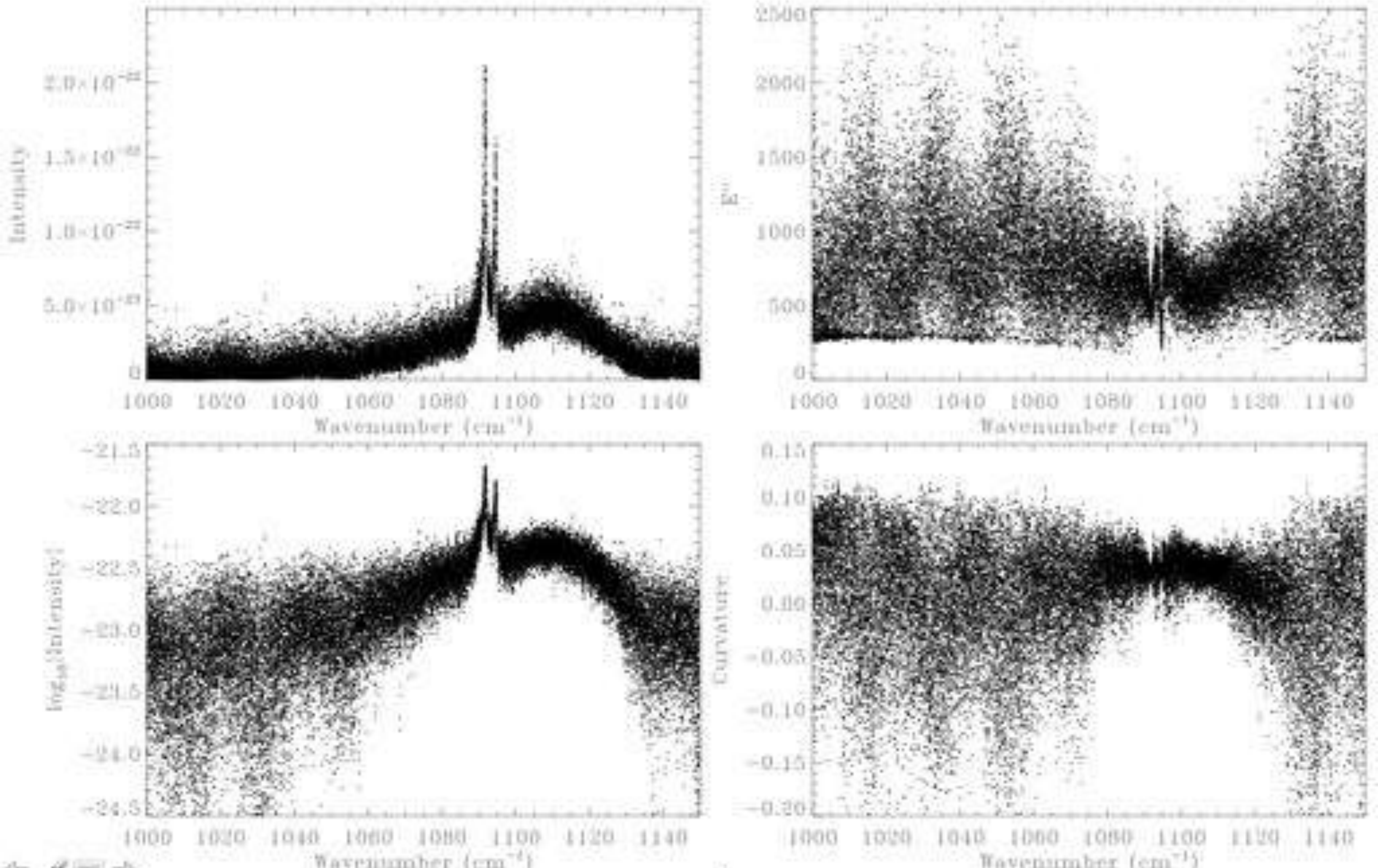
Derived Intensities & E” 700-830 cm^{-1}



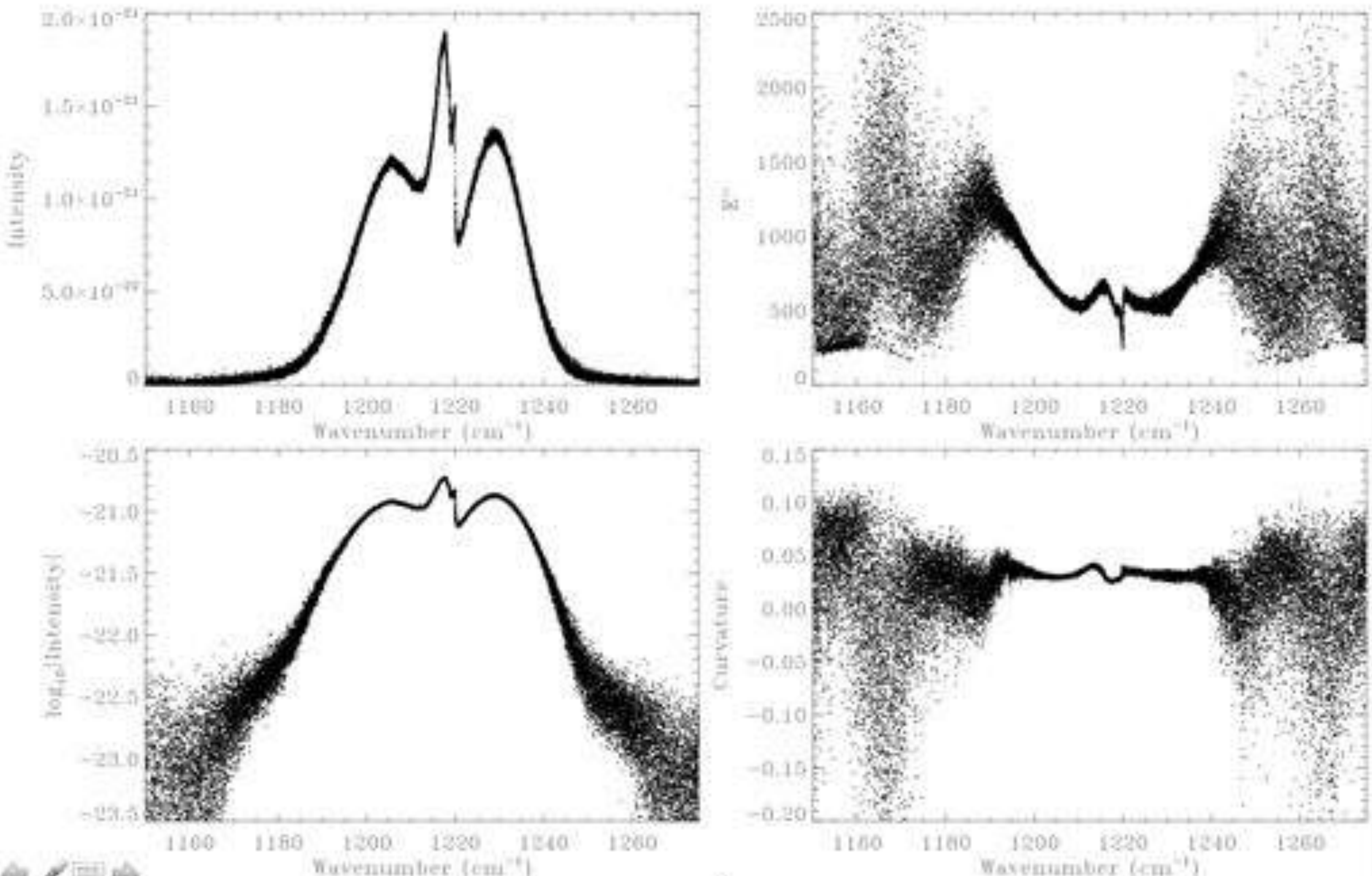
Derived Intensities & E” 830-999 cm^{-1}



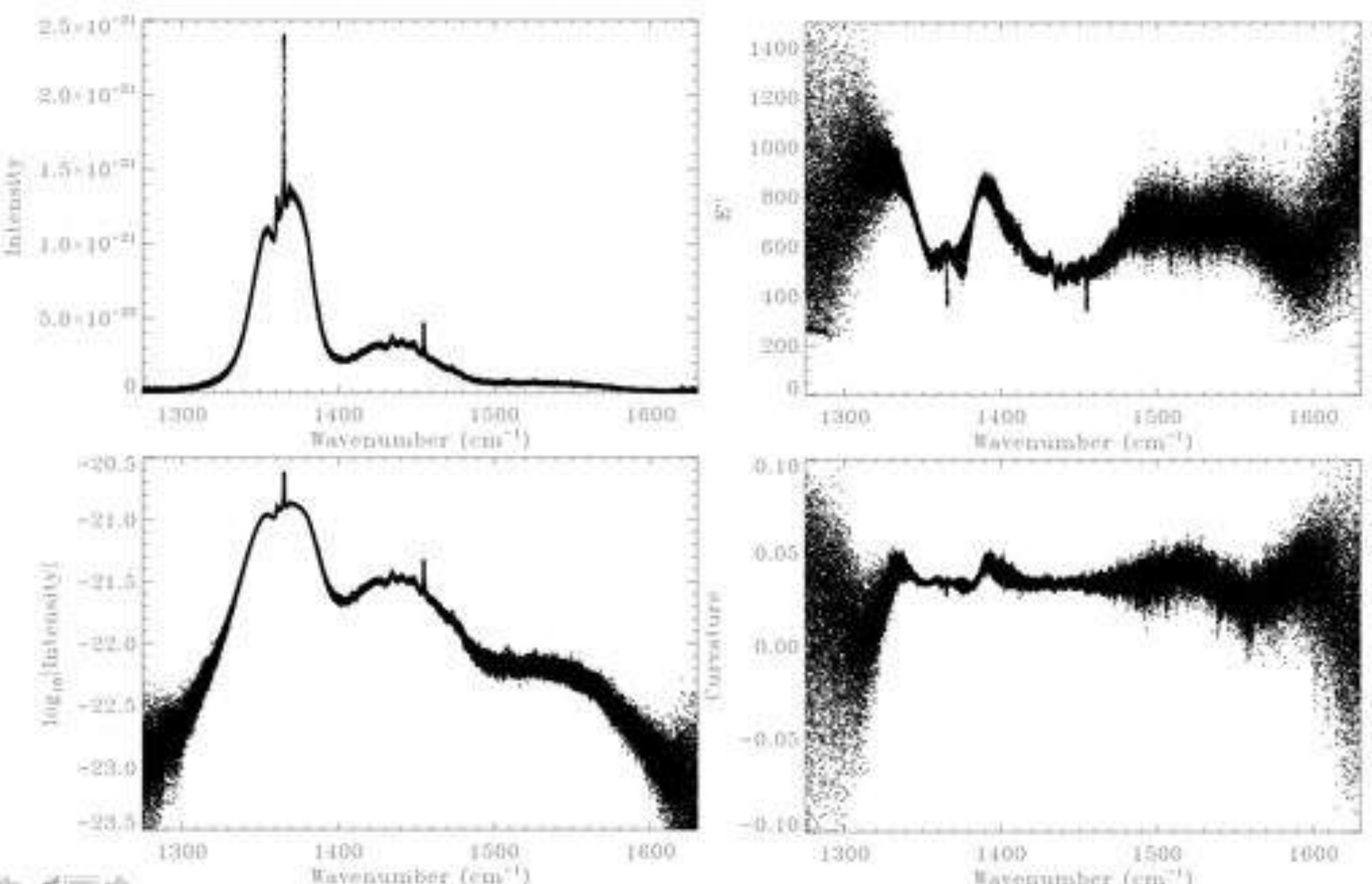
Derived Intensities & E” 1000-1150 cm^{-1}



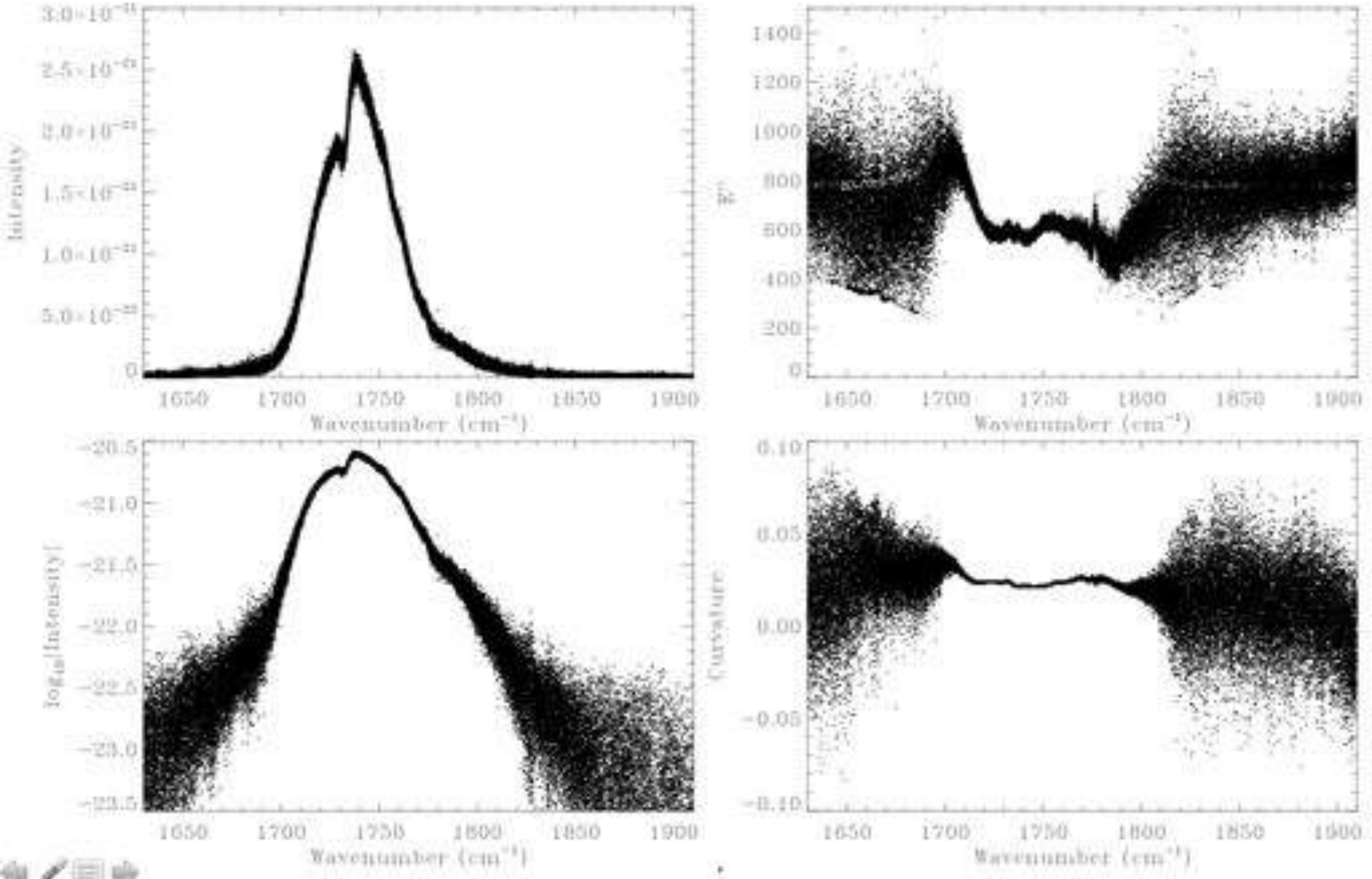
Derived Intensities & E” 1150-1275 cm^{-1}



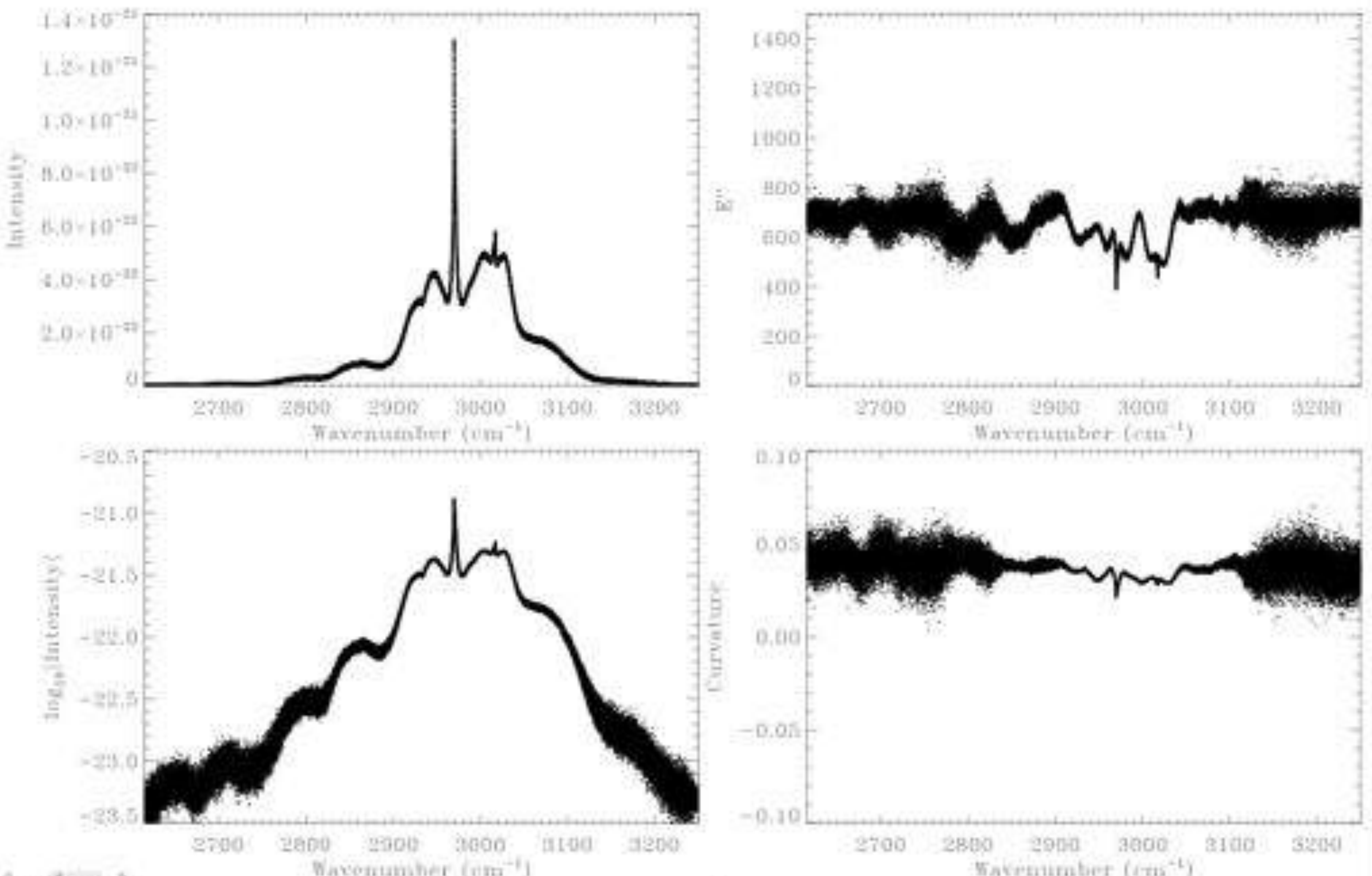
Derived Intensities & E” 1275-1630 cm^{-1}



Derived Intensities & E” 1630-1910 cm^{-1}



Derived Intensities & E” 2615-3250 cm^{-1}



Summary / Discussion

An empirical pseudo-linelist has been developed covering 700-1910 and 2615-3250 cm^{-1}, at a line spacing of 0.005 cm^{-1}, giving a total of 305,502 lines.

Four different lab data-sets were used: Harrison 2011a, Harrison 2011b, Waterfall, and PNNL, containing a total of 32 spectra.

ABHW were assumed to be 0.05 cm^{-1} / atm
SBHW were assumed to be 0.08 cm^{-1} / atm
A T-dependence of 0.5 was assumed for ABHW and SBHW.
Line intensities and E"s were derived from fitting all spectra simultaneously

A broad minimum of 0.95 was observed in the VSFs at ~250 K and maxima of 1.06 at 190 K and 290K. At 323 K the VSFs were ~1.3 implying missing hot-bands in the PLL. So this PLL is unsuitable for high-T use. But at the temperatures experienced by acetone in the Earth's atmosphere (200-290K), the error associated with using this PLL will never be more than 5%.

Although not the strongest band in terms of integrated area, the overlapping v_5 and v_{16} band has a sharp Q-branch at 1365 cm^{-1}, which offers the best spectral contrast in the IR.

NASA sponsorship acknowledged.