CFH_2CF_3 (HFC-134a) Pseudo-Line-List

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Six data-sets of laboratory spectra, downloaded from the HITRAN website, have been used to generate an empirical pseudo-linelist. Transmission spectra, generated from the lab cross-section data, were fitted simultaneously in order to minimize residuals between the lab spectra and synthetic spectra calculated from the PLL. In some spectral regions up to 70 spectra were used.

Available Laboratory Spectra

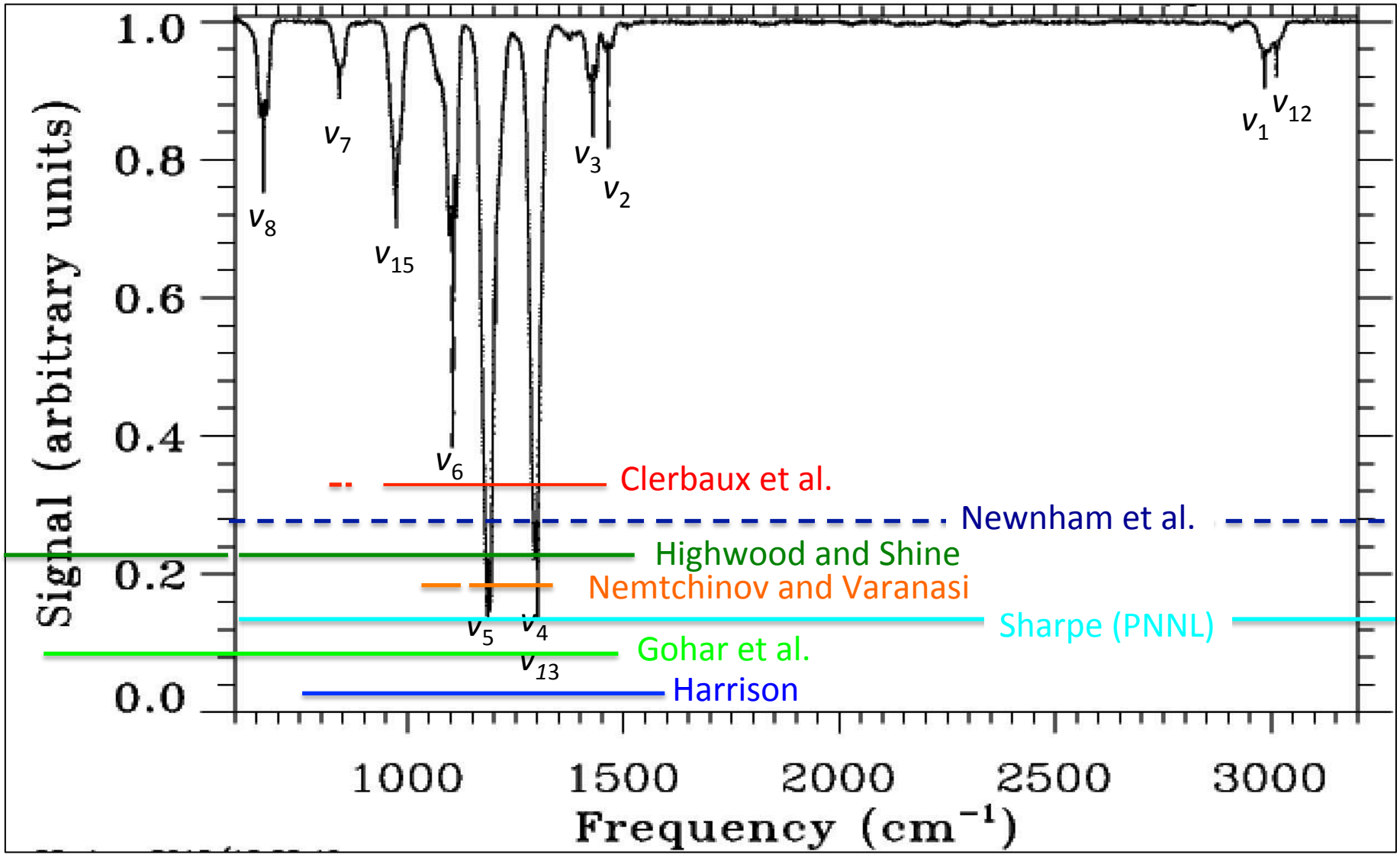
Seven different CFH_2CF_3 spectral datasets have been measured. Six of these were down-loaded from the HITRAN website and used to derive the PLL. Preference was given to those in the supplemental folder, where the –ve absorption coefficients have not been zeroed.

#	Reference	Range (cm^{-1})	Temp (K)	Pres (Torr)	Applied Scaling	N_s
A	Clerbaux et al. [1993]	815- 865 935-1484	253-287		0.72	0/3 3/3
B	Newnham et al. [1996]	600-3500	203-294	38-760	-	0/3
C	Highwood and Shine, [2000]	75 - 590 600-1540	253 253	< 1 < 1	1.00	1/1 1/1
D	Nemtchinov and Varanasi [2004]	1035-1130 1135-1340	180-297	< 1 < 1	1.00	32/49 33/49
E	Sharpe et al. [2004]	600-5000	278-323	760	1.00	3/3
F	Gohar et al. [2004]	300-1550	296	700	0.95	1/1
G	Harrison [2015]	750-1600	191-296	24-760	1.00	27/27

Footnotes:

1. Newnham et al. are included in the table for completeness; the spectra are missing from the HITRAN website and were therefore not used in the derivation of the PLL.
2. Only 32½ of 49 tabulated Nemtchinov spectra are available from HITRAN: all the lowest-P spectra at each temperature are missing, as are the all the lowest-T (180K) spectra.
3. The Clerbaux's spectra covering 815-865 cm^{-1} were too narrow and too noisy to be useful.

Sharpe et al. (PNNL) 278K spectrum



Illustrating main absorption bands of CFH_2CF_3 and the coverage of the laboratory spectra

Twelve Fitted Windows

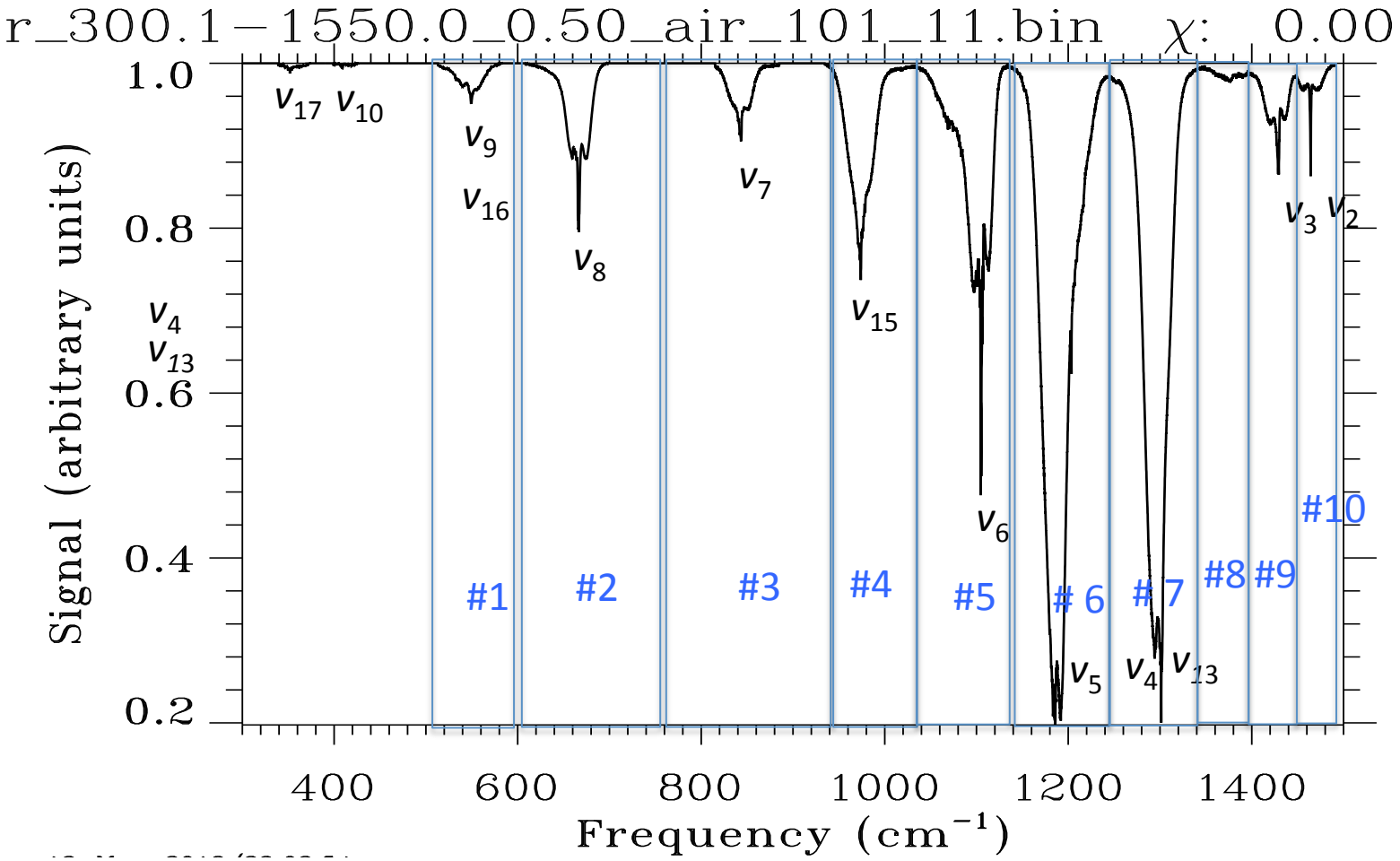
Defined 12 windows, each centered on an absorption band. Chose each window based on three criteria:
1) Boundaries in regions of weak absorption
2) Maximize utilization of the various datasets
3) Maximize spectral coverage

The right-most column (N_S) shows the total number of spectra that were fitted in each window. In total 412 spectral fits were performed out of a potential 103 x 12 = 1236

Although there are absorption bands visible below 500 cm^{-1} in the spectrum of Highwood and Shine, these are substantially weaker than the v_9 band centered at 549 cm^{-1}. Based on their weakness and the very limited lab spectra, it was decided not to extend the PLL below 500 cm^{-1}

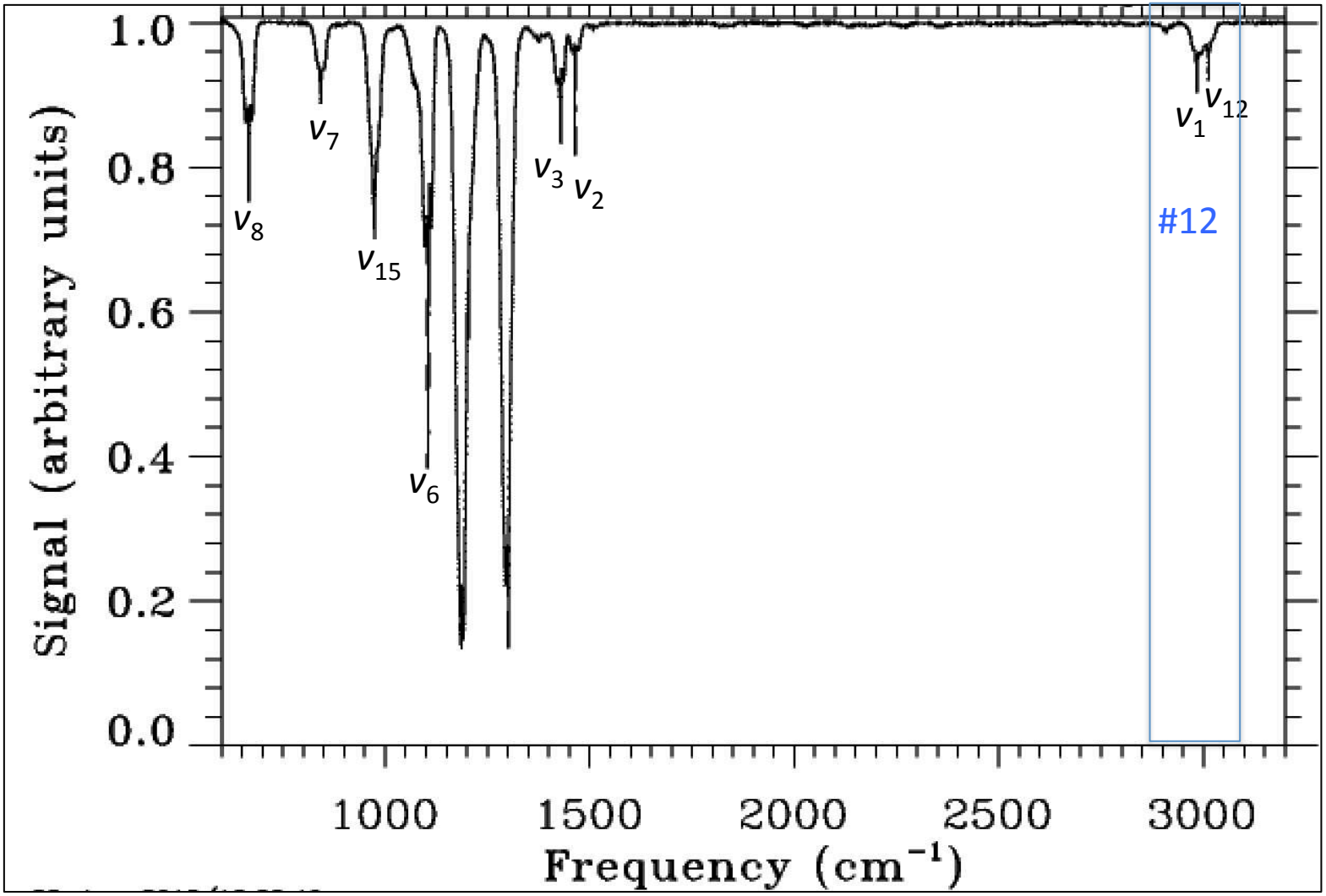
#	Center (cm^{-1})	Width (cm^{-1})	Datasets covered	N_S
1	548.00	83.00	C F	2
2	676.05	147.90	C EF	5
3	845.00	189.55	C EFG	34
4	987.50	95.00	A C EFG	37
5	1082.50	94.15	A CDEFG	68
6	1189.00	107.15	A CDEFG	70
7	1291.50	96.15	A CDEFG	69
8	1368.05	56.90	A C EFG	37
9	1421.60	50.20	A C EFG	37
10	1465.15	36.90	A C EFG	37
11	1511.75	55.50	C E G	33
12	2920.00	260.00	E	3

Gohar et al. 278K spectrum



Illustrating main absorption bands, and fitted windows (#). Due to the weakness of the bands below 500 cm^{-1}, and the sparsity of the lab spectra, the PLL was not extended below 500 cm^{-1}.

PNNL 278K spectrum



Illustrating main absorption bands. And the fitted windows (#).

Partition Function

For the vibrational partition function, the following 18 modes were used with the tabulated wavenumbers and degeneracies:

ν_1: 2981 1
ν_2: 1462 1
ν_3: 1428 1
ν_4: 1301 1
ν_5: 1185 1
ν_6: 1104 1
ν_7: 843 1
ν_8: 666 1
ν_9: 549 1
ν_{10}: 408 1
ν_{11}: 225 1
ν_{12}: 3010 1
ν_{13}: 1294 1
ν_{14}: 1191 1
ν_{15}: 973 1
ν_{16}: 540 1
ν_{17}: 358 1
ν_{18}: 110 1

A molecular weight of 102 was used.

A rotational partition function of $(296/T)^{1.5}$

A residual T-dependence of 5% was implemented.

These values are based on the paper on the following page.

Ab Initio Calculations of Vibrational Frequencies and Infrared Intensities for Global Warming Potential of CFC Substitutes: CF_3CH_2F (HFC-134a)

Stella Papasavva, Stephanie Tai, Amy Esslinger, Karl H. Illinger,* and Jonathan E. Kenny*

TABLE 1: Previous Assignments of the Fundamental Frequencies (cm^{-1}) of CF_3CH_2F (Vapor State Values Given Except Where Noted)

	experimental (vapor state)			force field
	infrared, Raman[a]	infrared, Raman[b]	infrared[c]	calculated[d]
A′				
ν_1	2984	2984	2986	2984
ν_2	1431	1464	1427	1431
ν_3	1296	1427	1296	1371
ν_4	1096	1298	1186	1298
ν_5	1067	1103	1103	1191
ν_6	908	972	1070	1096
ν_7	843	843	846	853
ν_8	666	665	666	661
ν_9	550	549	557	546
ν_{10}	358[e]	408	410	385
ν_{11}	201	225	222	246
A″				
ν_{12}	3015	3013	3015	3015
ν_{13}	1374	1182	1463	1302
ν_{14}	1189	665	1296	1199
ν_{15}	972	539	971	967
ν_{16}	541	352	542	545
ν_{17}	407[e]	225	358	358
ν_{18}	124[e]	120	112	139

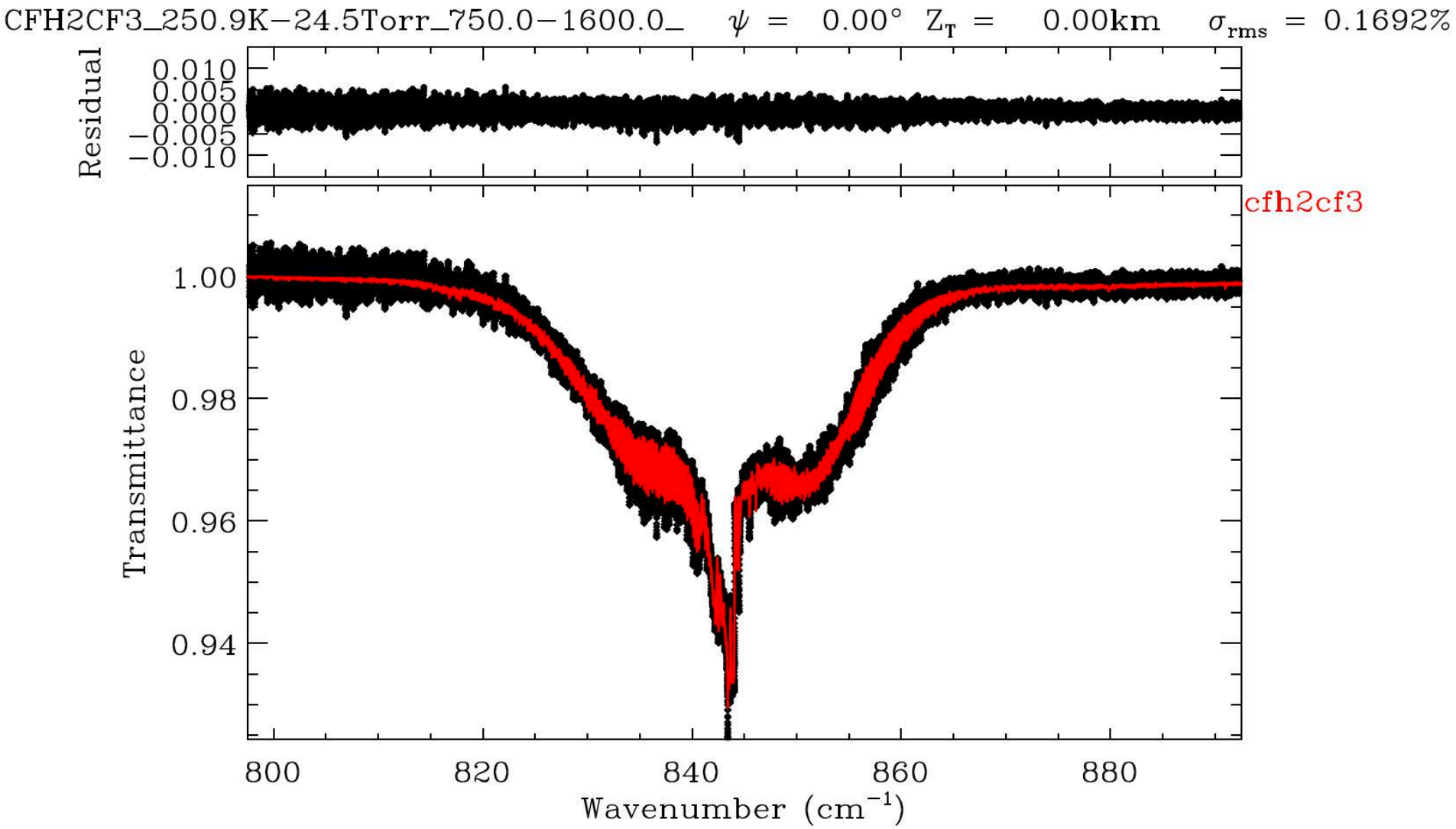
[a] Reference 4. [b] Reference 5. [c] Reference 6. [d] Reference 7. [e] Frequency assigned from Raman spectrum taken in the liquid state.

TABLE 3: Vibrational Frequencies (cm^{-1}) and Absolute Infrared Intensities (km/mol) of CF_3CH_2F Determined in This Work (Except for Experimental Values <400 cm^{-1})

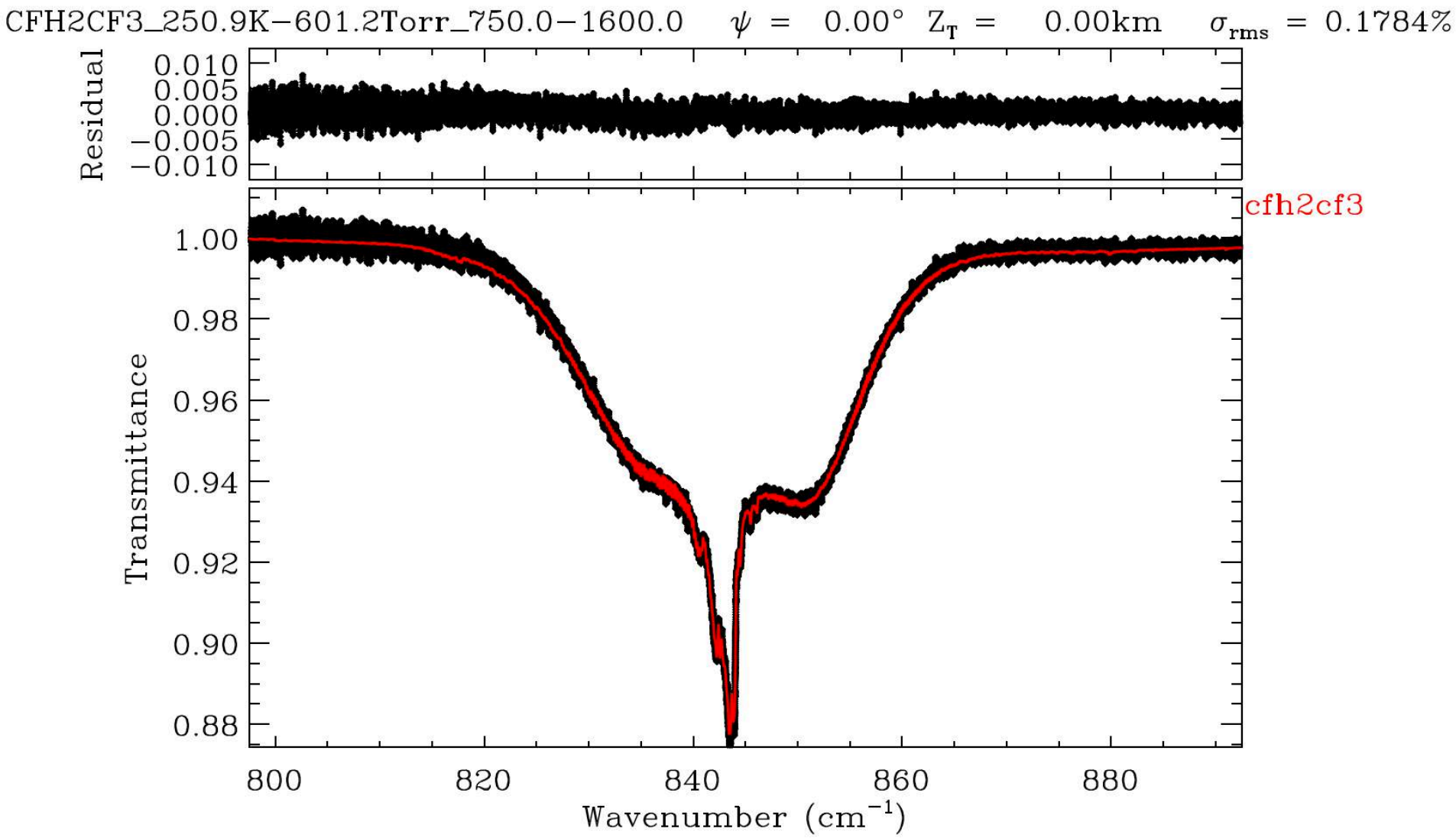
		ab initio MP2/6-31G**, GAUSSIAN 92		semiempirical PM3, HYPERCHEM 4	
vibration no.	experimental frequency	frequency	IR intensity	frequency	IR intensity
A′					
ν_1	2981	3169	13	3021	4
ν_2	1462	1563	5	1583	50
ν_3	1428	1508	23	1523	40
ν_4	1301	1363	140	1396	36
ν_5	1185	1246	262	1323	3
ν_6	1104	1147	70	1141	2
ν_7	843	865	19	898	0
ν_8	666	668	31	629	18
ν_9	549	549	9	523	9
ν_{10}	408	413	1	402	2
ν_{11}	225[a]	216	3	261	1
A″					
ν_{12}	3010	3245	14	2990	5
ν_{13}	1294	1360	143	1573	73
ν_{14}	1191	1247	63	1041	0
ν_{15}	973	1021	60	936	1
ν_{16}	540	530	3	501	4
ν_{17}	358[a]	358	1	357	0
ν_{18}	110[b]	114	5	92	2

[a] Reference 8. Values cited agree with most other reports. [b] Average of values reported in refs 6 and 8.

Example of Spectra fit to 251K, 25 Torr Harrison spectrum in Window #3



Example of Spectral fit to 251 K 601 Torr Harrison spectrum in Window #3



Removal of Biases

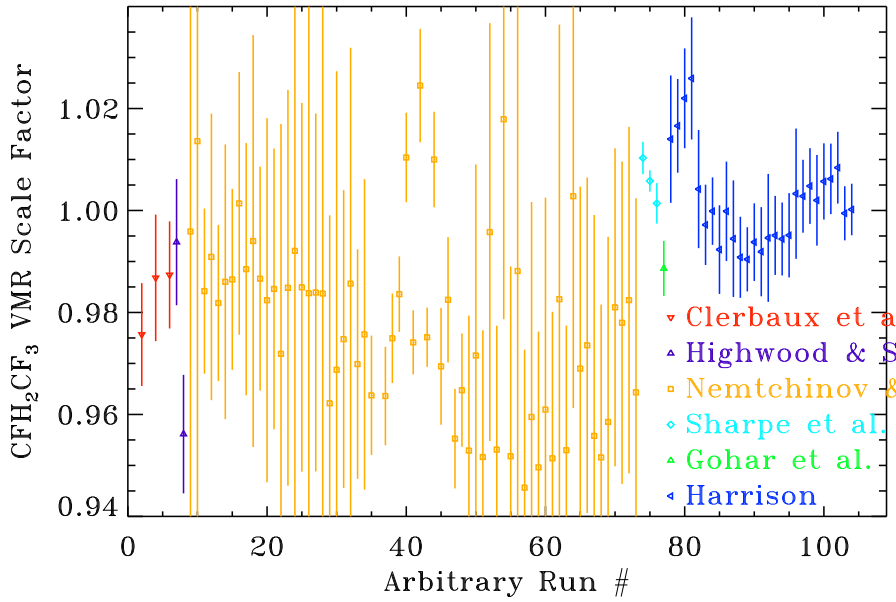
It is important that all the various spectra are brought into consistency, in terms of the absolute absorption cross-section and wavenumber calibrations, before a PLL is generated. Otherwise the biases will generate artifacts in the PLL parameters due to the different coverage (in terms of temperature, pressure, wavenumber) of the different data-sets.

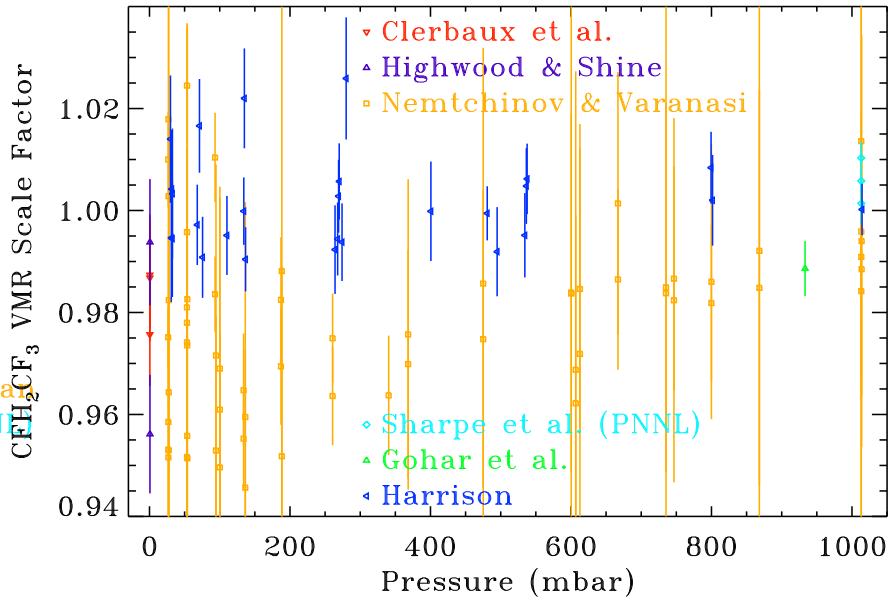
For example, if a data-set that was acquired only at low temperatures were biased low in terms of the absorption cross-sections, this would lead to a high bias in the overall derived E" values in the spectral regions covered by this erroneous data-set.

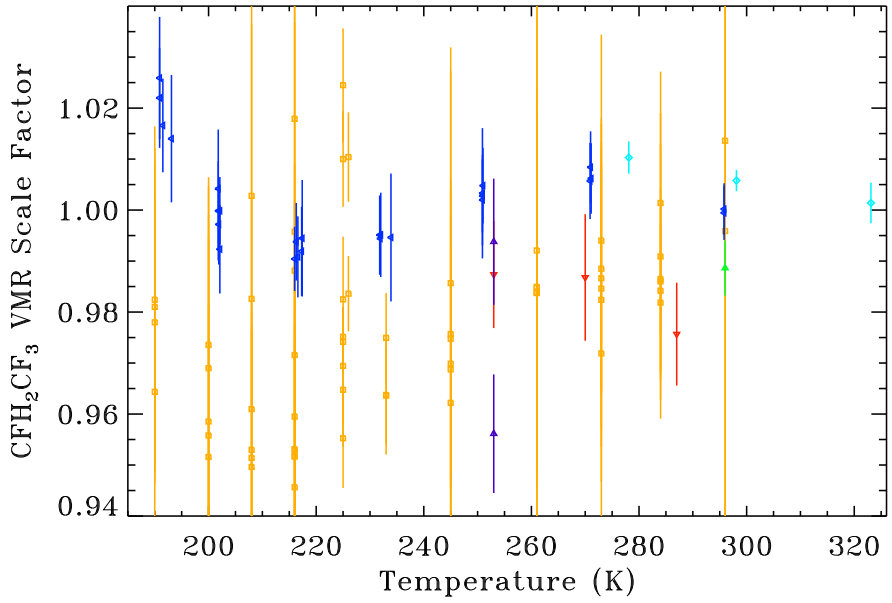
For this reason, there were adjustments made to the Clerbaux and Gohar cross-sections. The former were multiplied by 0.72 and the latter by 0.95 before use in deriving the PLL. The other four data-sets seems to be consistent within 5%.

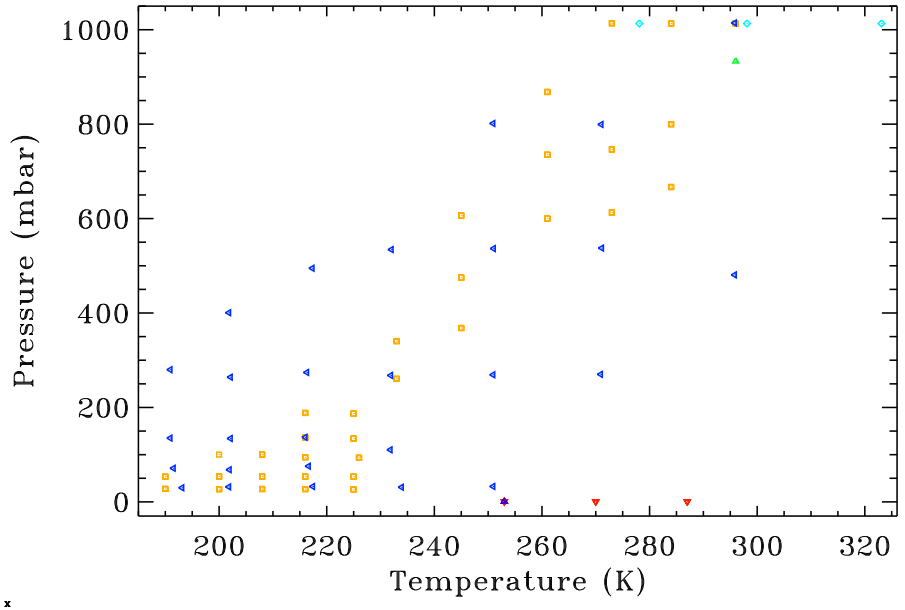
Subsequent plots show results **after** applying corrections to the cross sections and the wavenumber calibration.

Retrieved CFH_2CF_3 amounts (VSFs)









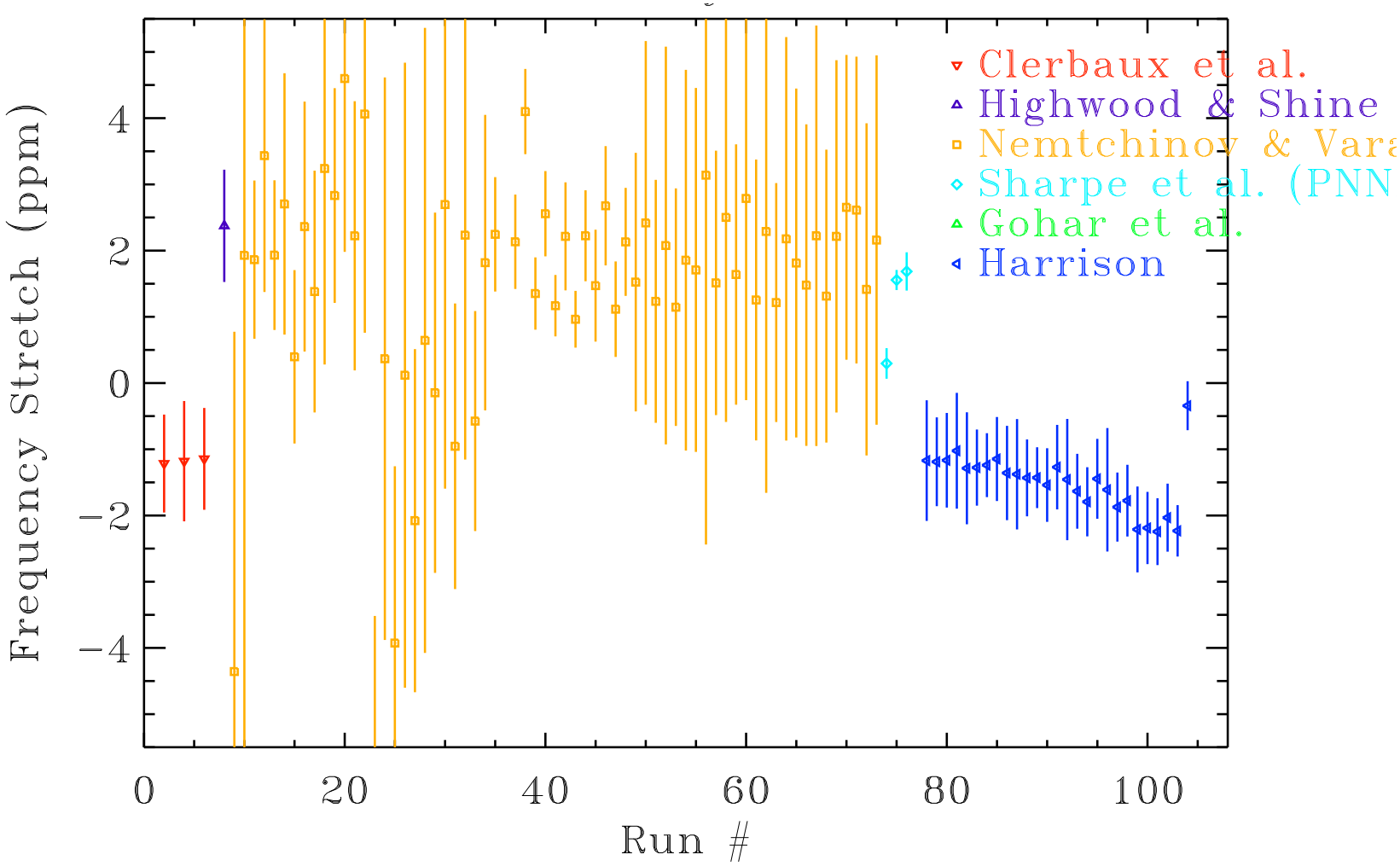
Discussion

Previous slide shows retrieved CFH_2CF_3 amounts, relative to the actual amount based on the measurement conditions, scaled by the correction factors on slide 2 (0.72 for Clerbaux et al., 0.95 for Gohar, and 1.0 for the others). These VMR Scale Factors (VSFs) would all be 1.0 in a perfect world. Data from all available windows are averaged for each spectrum, reducing the dimensionality of the problem, avoiding having 12 very similar plots – one for each window.

Retrieved CFH_2CF_3 amounts are generally consistent amongst measurements, with the exception of the Clerbaux data, which produce only 72% of the true gas amount, implying that the Clerbaux cross-sections are too large.

Curvature in the T-dependence of the VMR scale factors was observed to be ±5% with a minimum at 250K was also corrected by application of an extra correction factor. This correction had already been applied in the previous plot. This curvature is very likely to be due to hot-bands of significant strength underlying the fundamentals, which invalidate the basic assumption that a single line can represent the absorption at each wavenumber.

Retrieved Frequency Stretches (ppm)



A wavenumber stretch of 2 ppm corresponds to 0.002 cm^{-1} at 1000 cm^{-1}

Summary

Six different lab spectral datasets of CFH_2CF_3 absorption have been fitted simultaneously to generate a single PLL to represent their absorption.

103 spectra were fitted over 12 different windows. Out of the 1236 potential spectral fits, only 412 could actually be performed. This was mainly due to the limited coverage of many spectra and a few data quality issues.

The resulting pseudo-linelist contains:

- 209,201 lines covering 504-1550 cm^{-1} at 0.005 cm^{-1} spacing
- 26,001 lines covering 2790-3050 cm^{-1} at 0.010 cm^{-1} spacing

235,202 total lines

The linelist uses the old HITRAN 2000 format with 100 characters per line.

Gas # 76 was arbitrarily assigned to CFH_2CF_3 with isotopolog #0. The former can be changed.

Future Work

1) Get hold of the Newnham et al. cross-sections and include in a future –re-analysis.

2) Try to find missing Nemtchinov & Varanasi spectra and include in a future re-analysis.

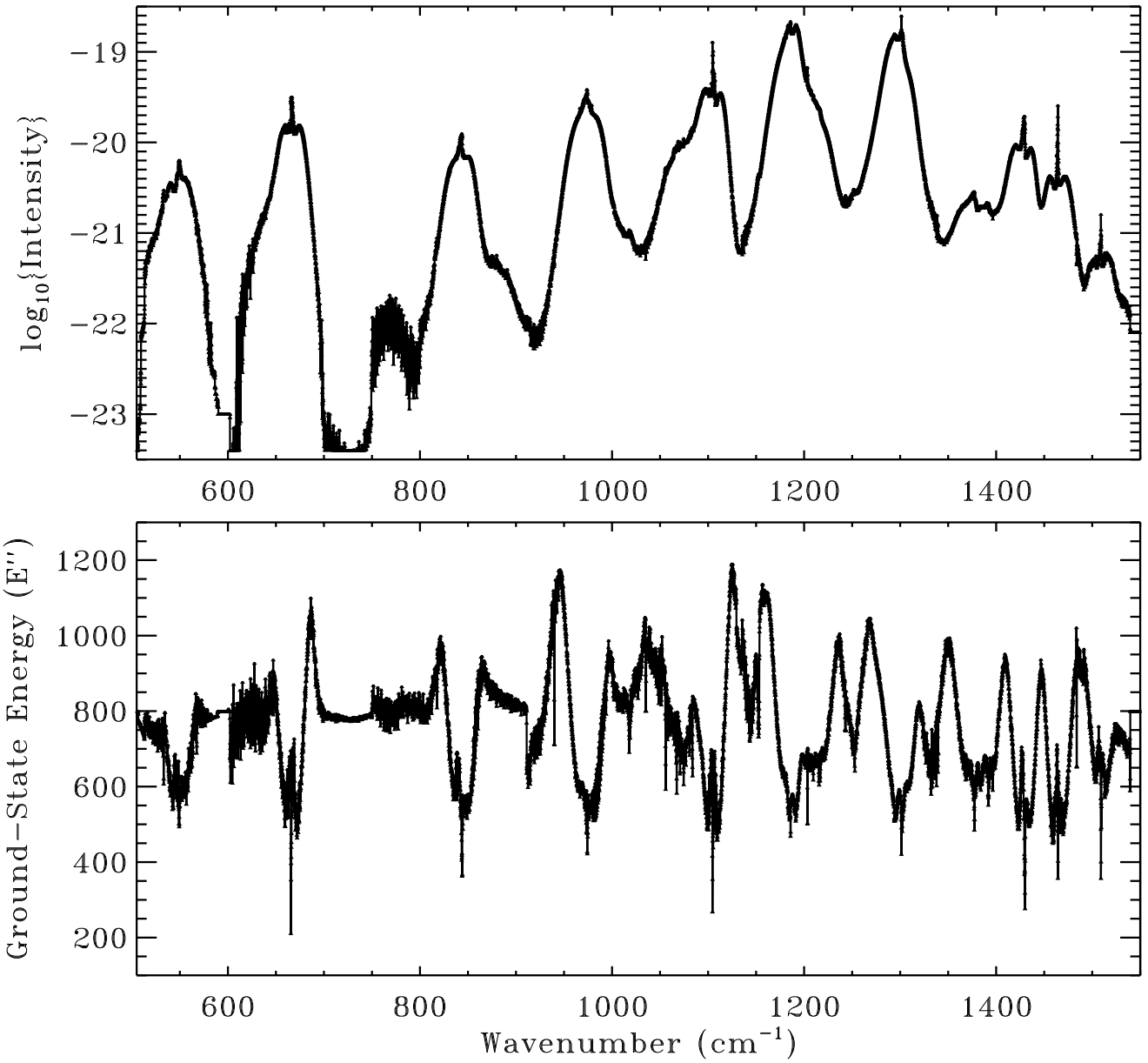
3) Although the Gohar et al. spectral cross-sections start at 300 cm^{-1}, they are actually all zero up to 339 cm^{-1}. Similarly, although the Gohar spectrum nominally extends to 1550 cm^{-1}, beyond 1490 cm^{-1} it is all zeros. There are also zeros between all the bands including the 374-399 and 426-513 cm^{-1} regions. The latter causes a problem because the PLL starts at 504 cm^{-1}. GFIT assumes that the Gohar cross-section is really zero below 513 cm^{-1}, which biases the PLL strengths low and creates artifacts in the derived E" and curvature.

Not sure of the origin of these zeros. Perhaps the cross-sections went negative and were set to zero. So It might be better to chop up the Gohar spectrum into multiple slices with non-zero cross-sections, discarding the regions where the cross-sections are zero. This way, GFIT won't be able to fit the zeroed regions, preventing biasing the PLL intensities.

4) Although the Highwood & Shine absorption spectrum nominally covers 600-1540 cm^{-1}, it is actually zero between 700-753 cm^{-1}, 913-942 cm^{-1} and other places.

5) Investigate noisy patch in Intensities and E" from 650-700 cm^{-1}. Is it simply a lack of noise above 700 cm^{-1} due to the Highwood & Shine cross-sections being set to zero there?

Properties of PLL in 0.1 cm^{-1} bins



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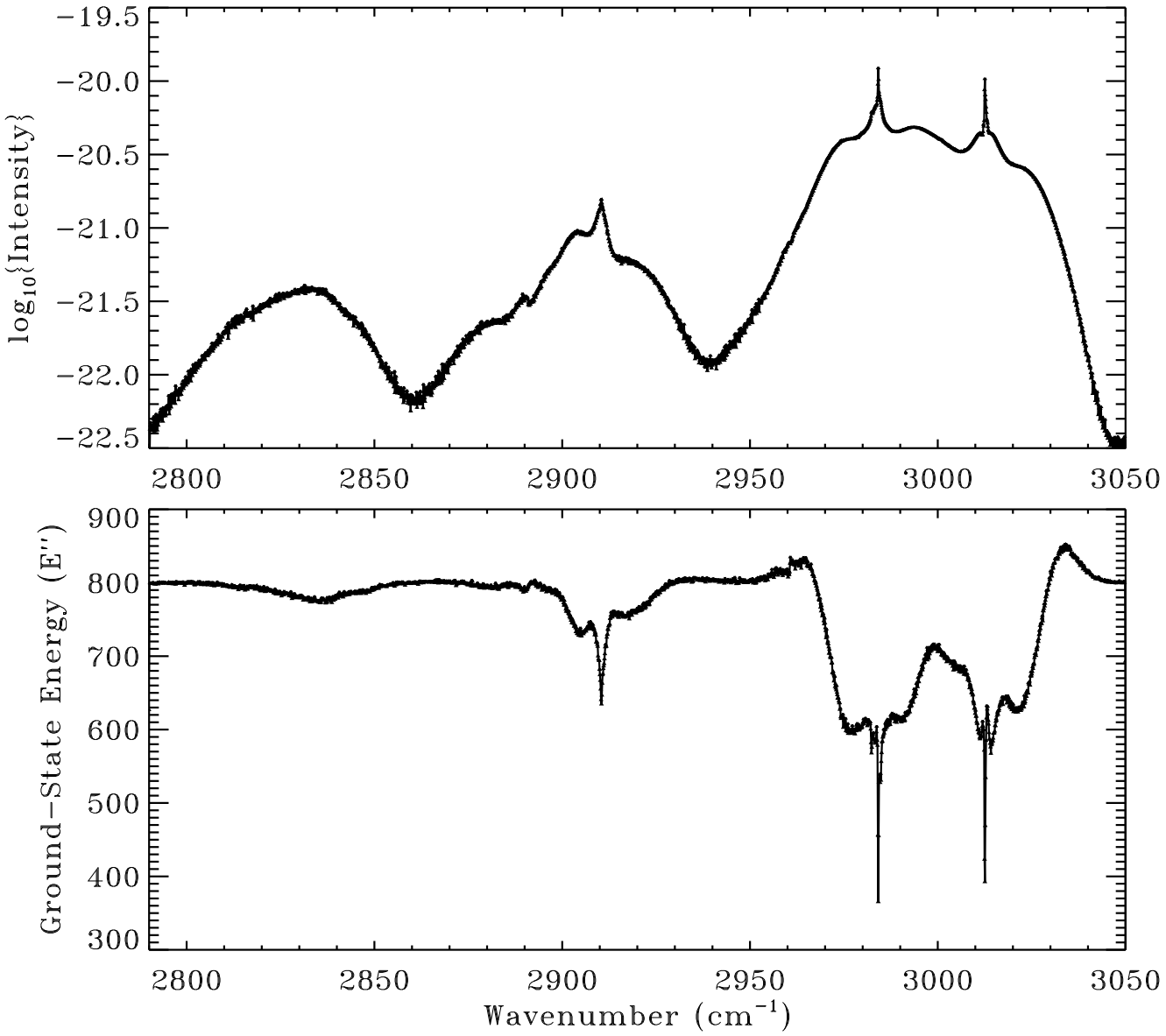
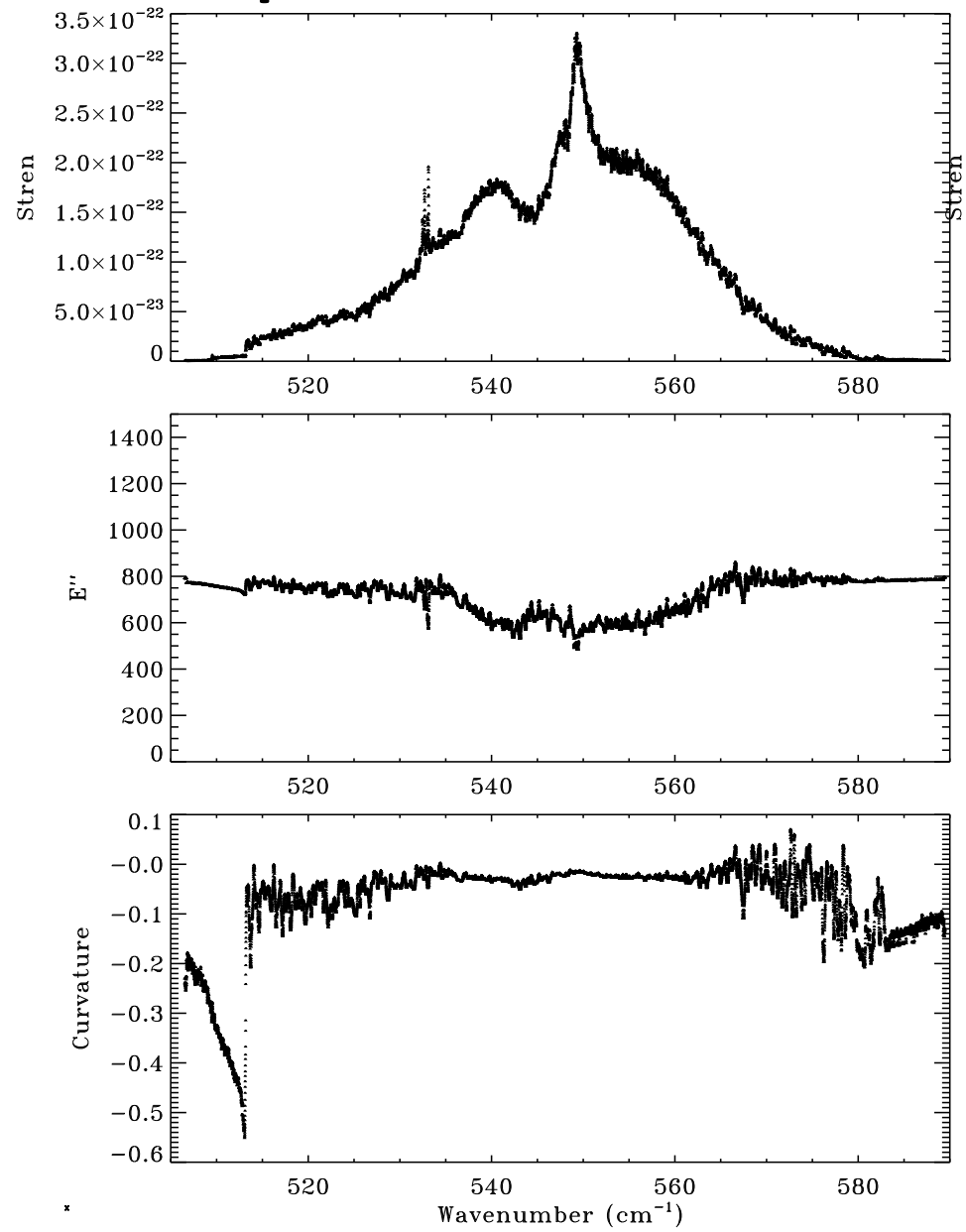
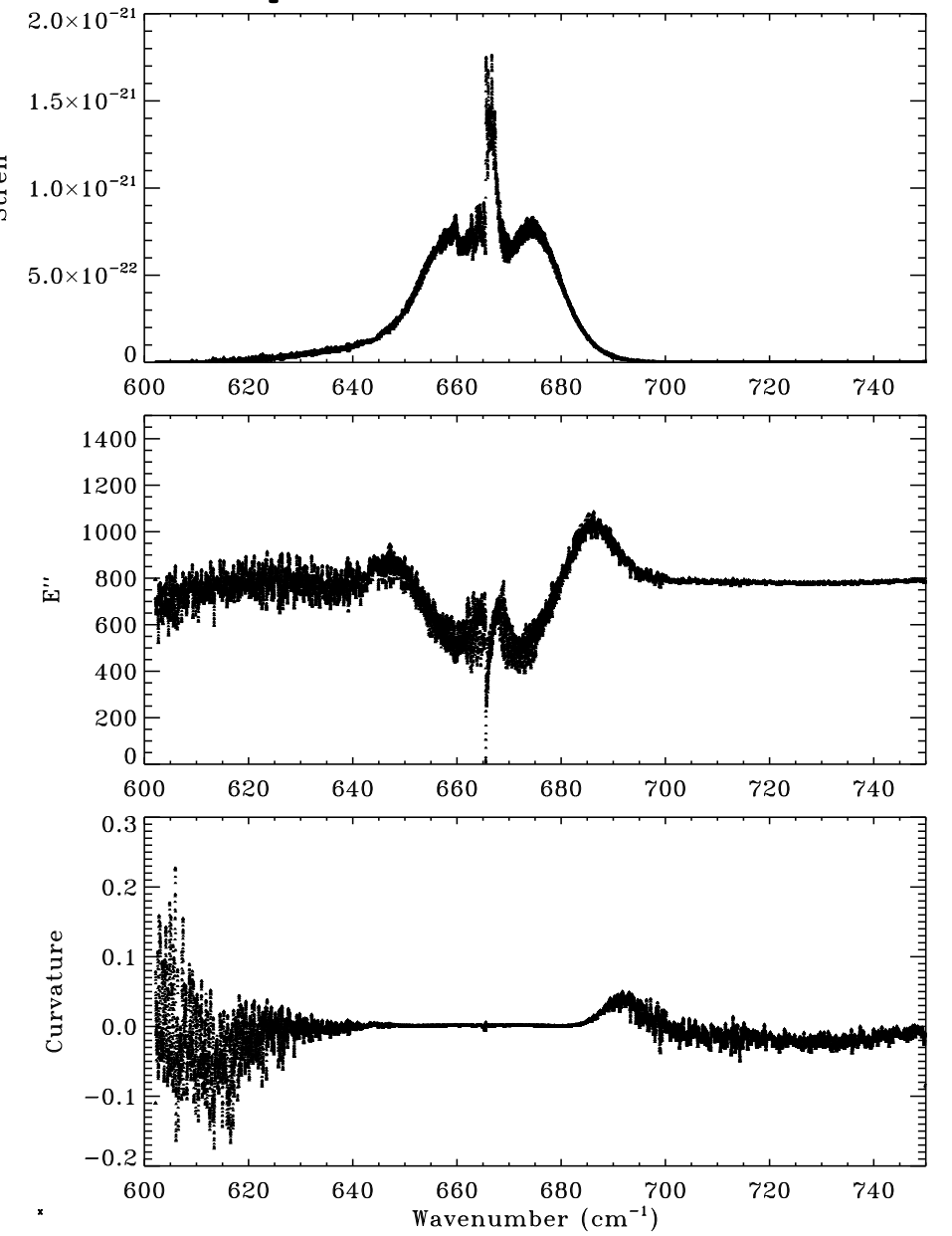


Properties of individual pseudo-lines





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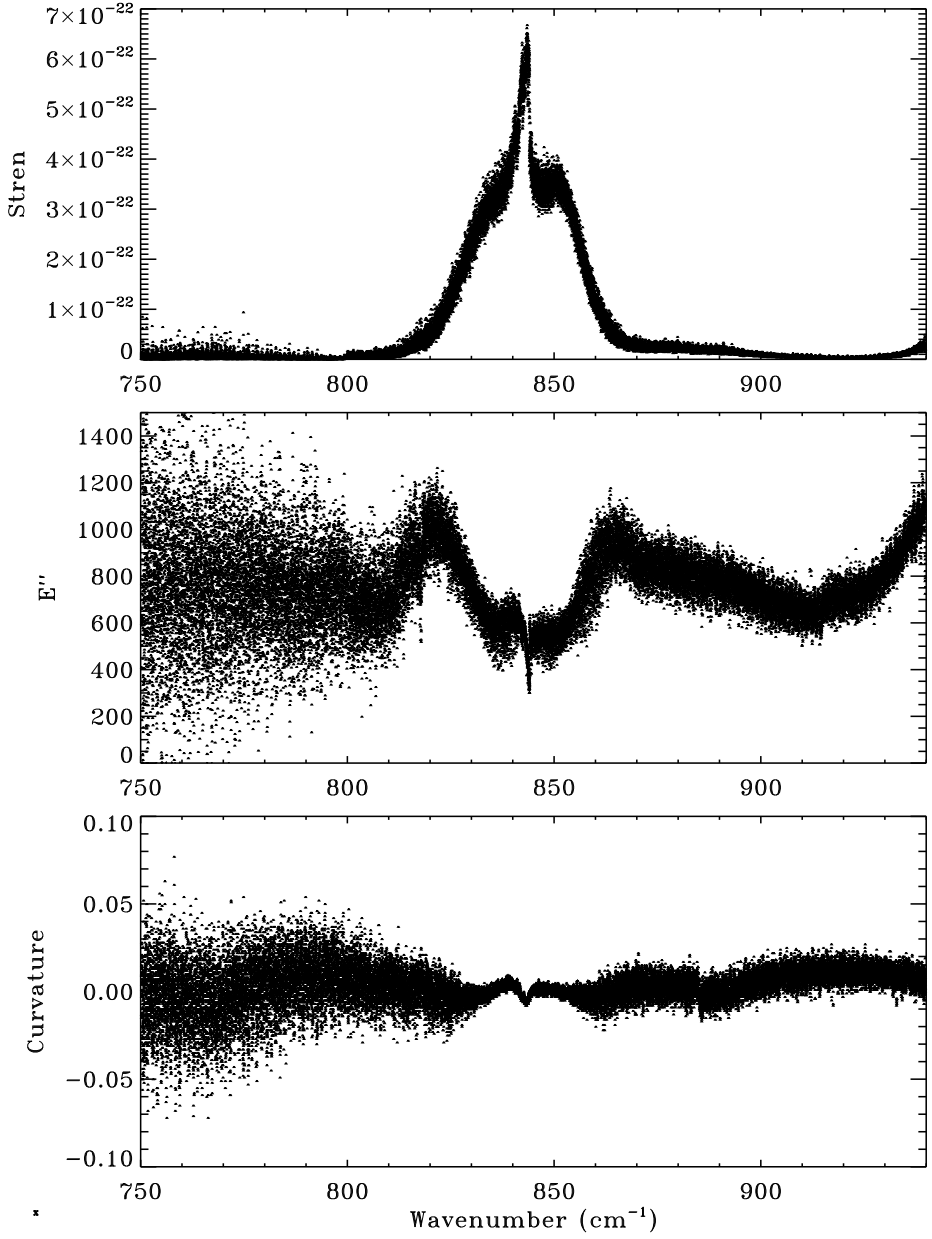

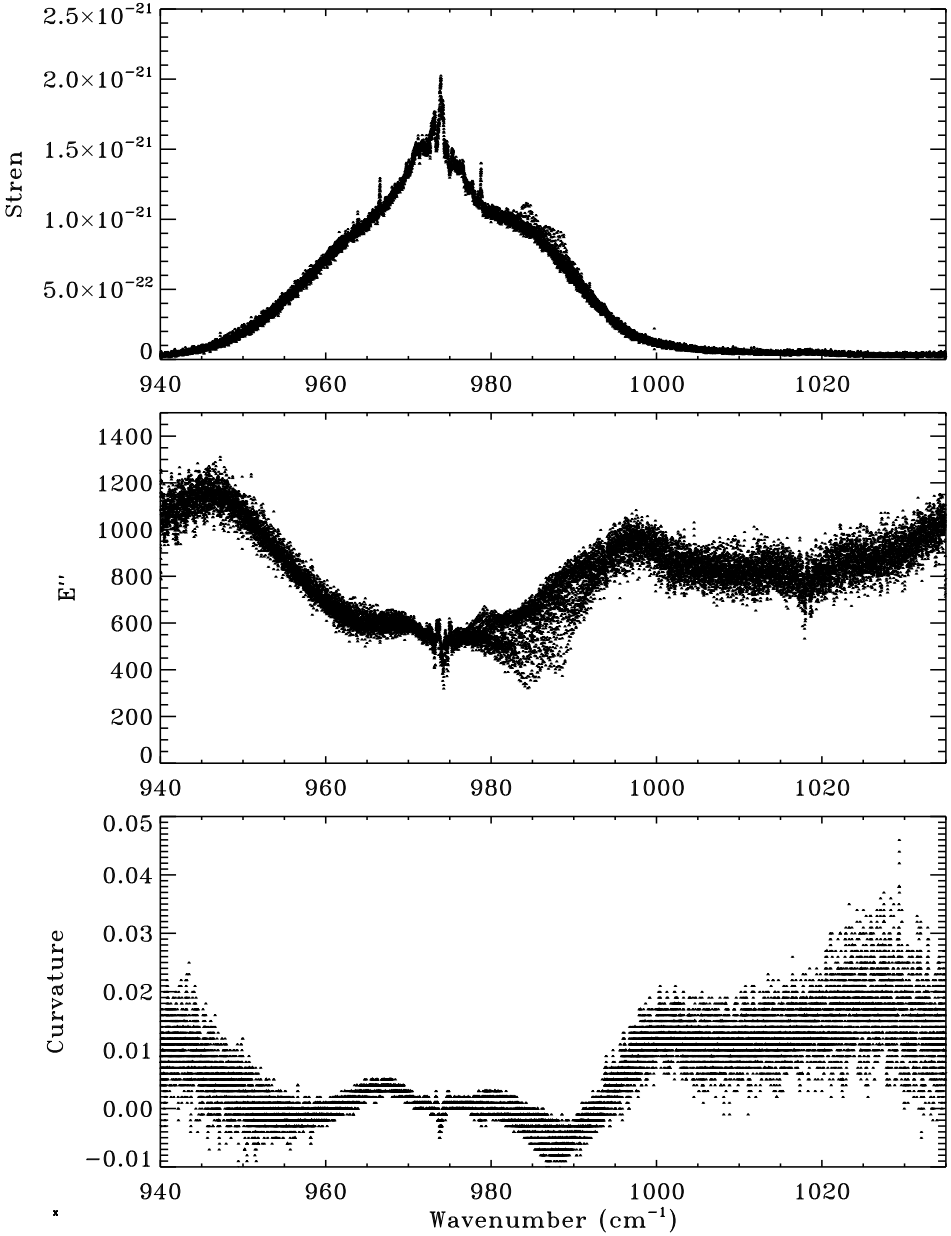

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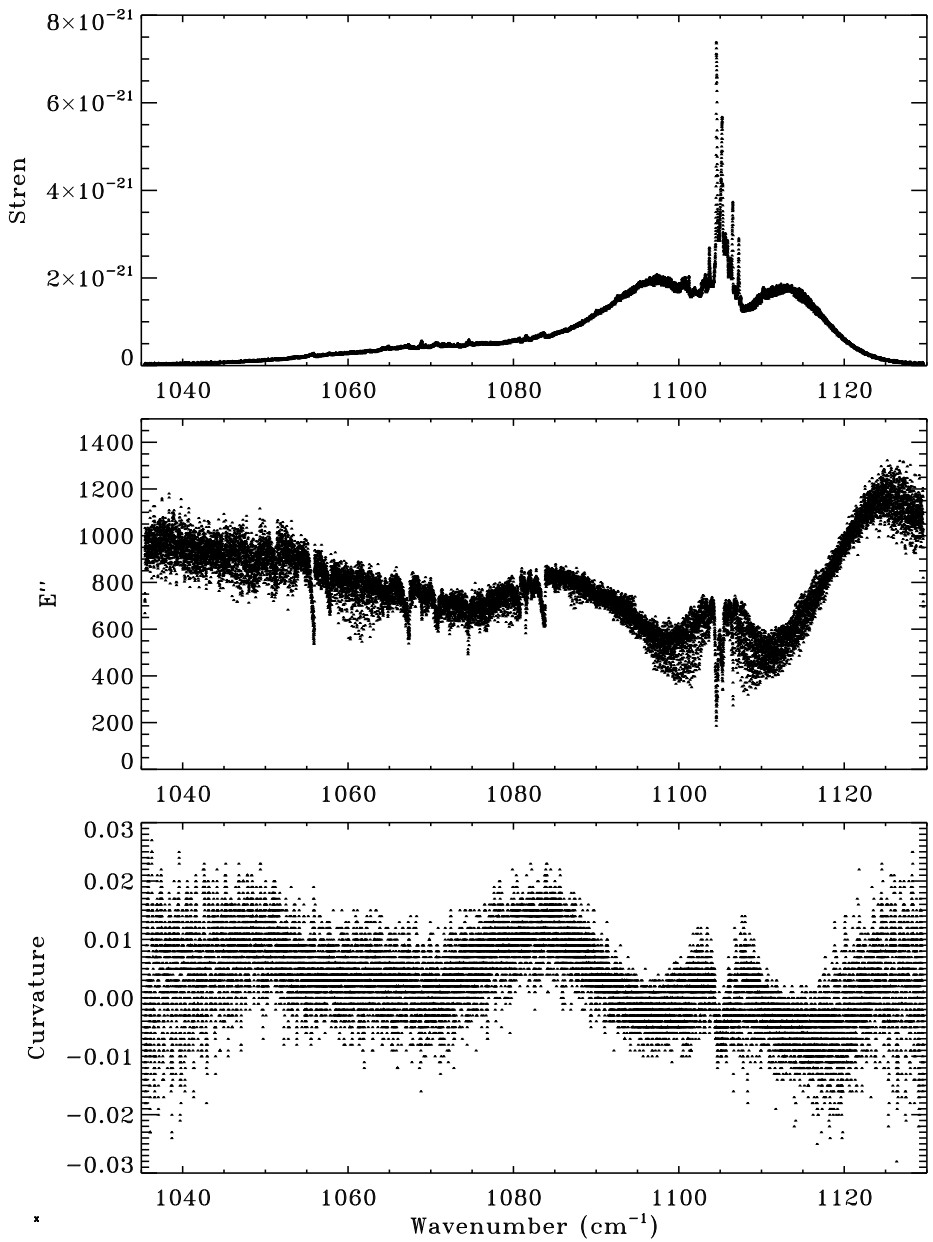

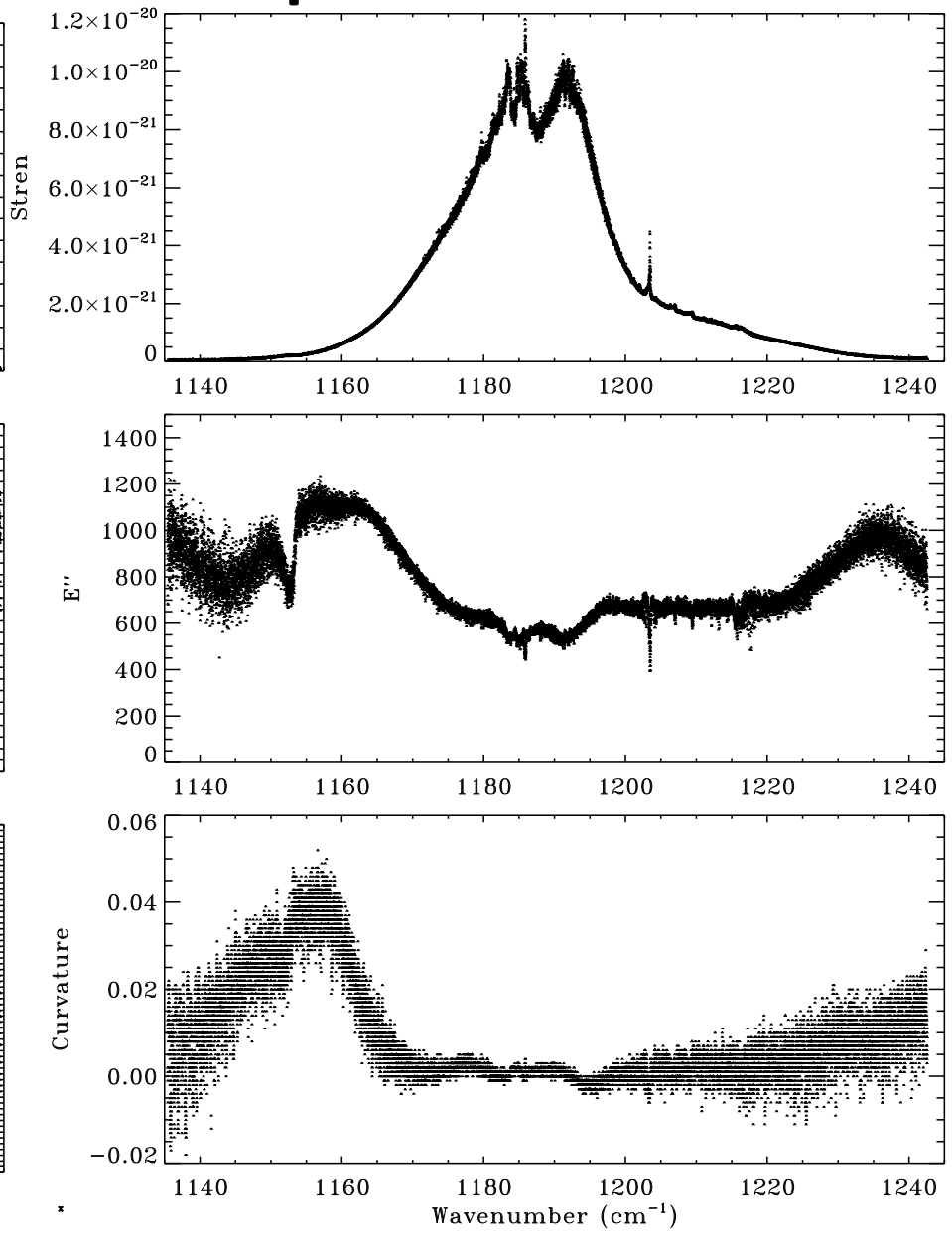

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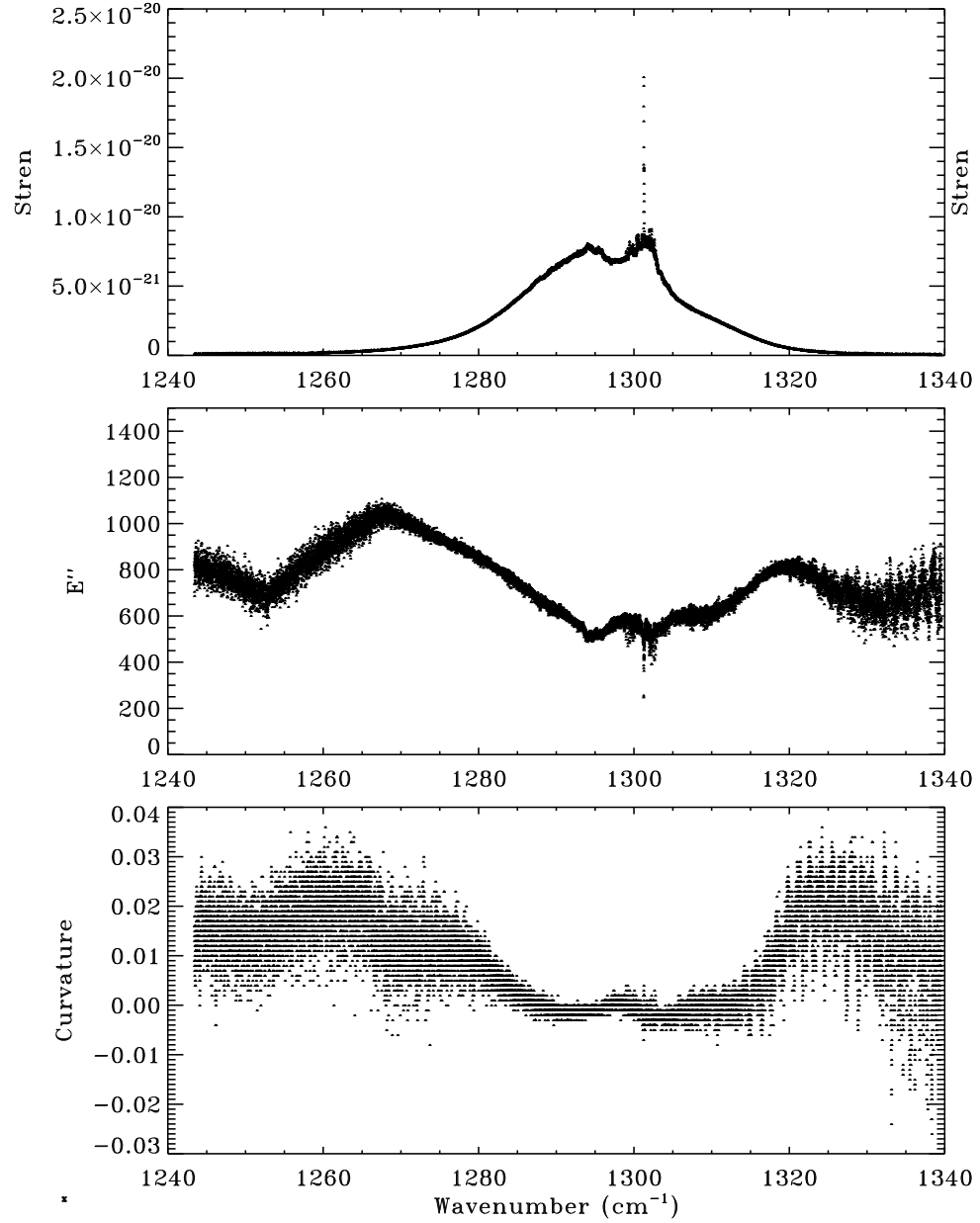

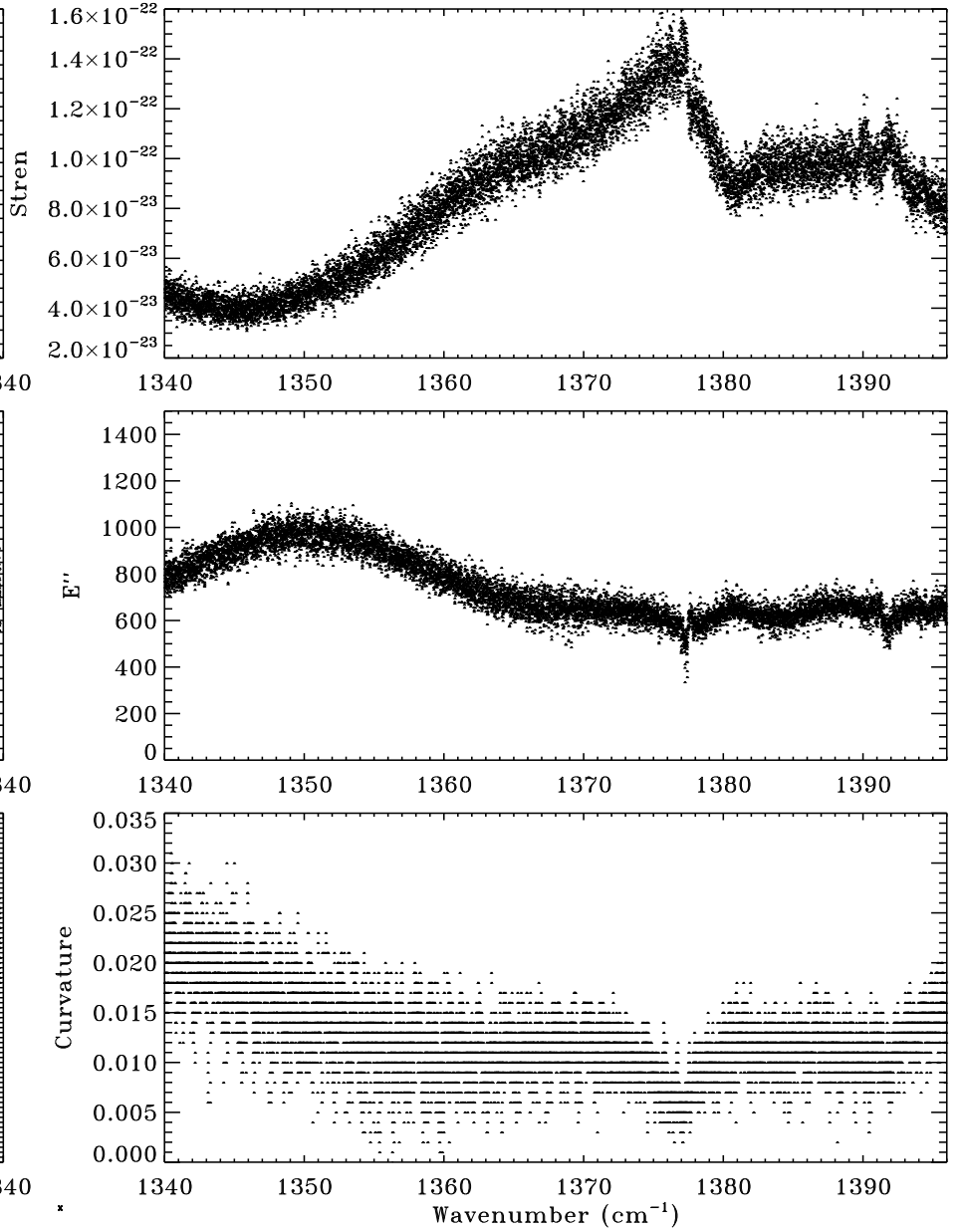

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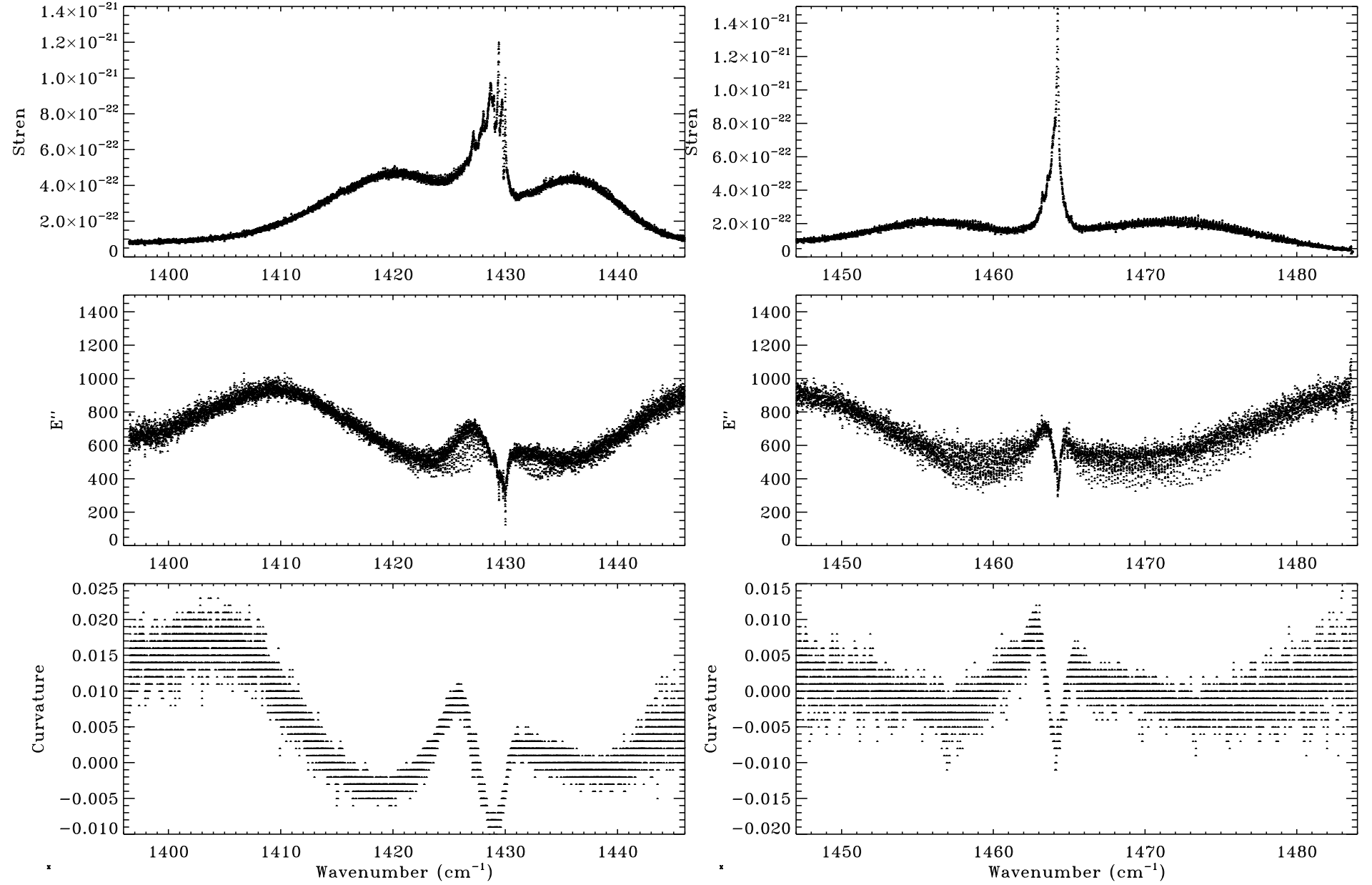
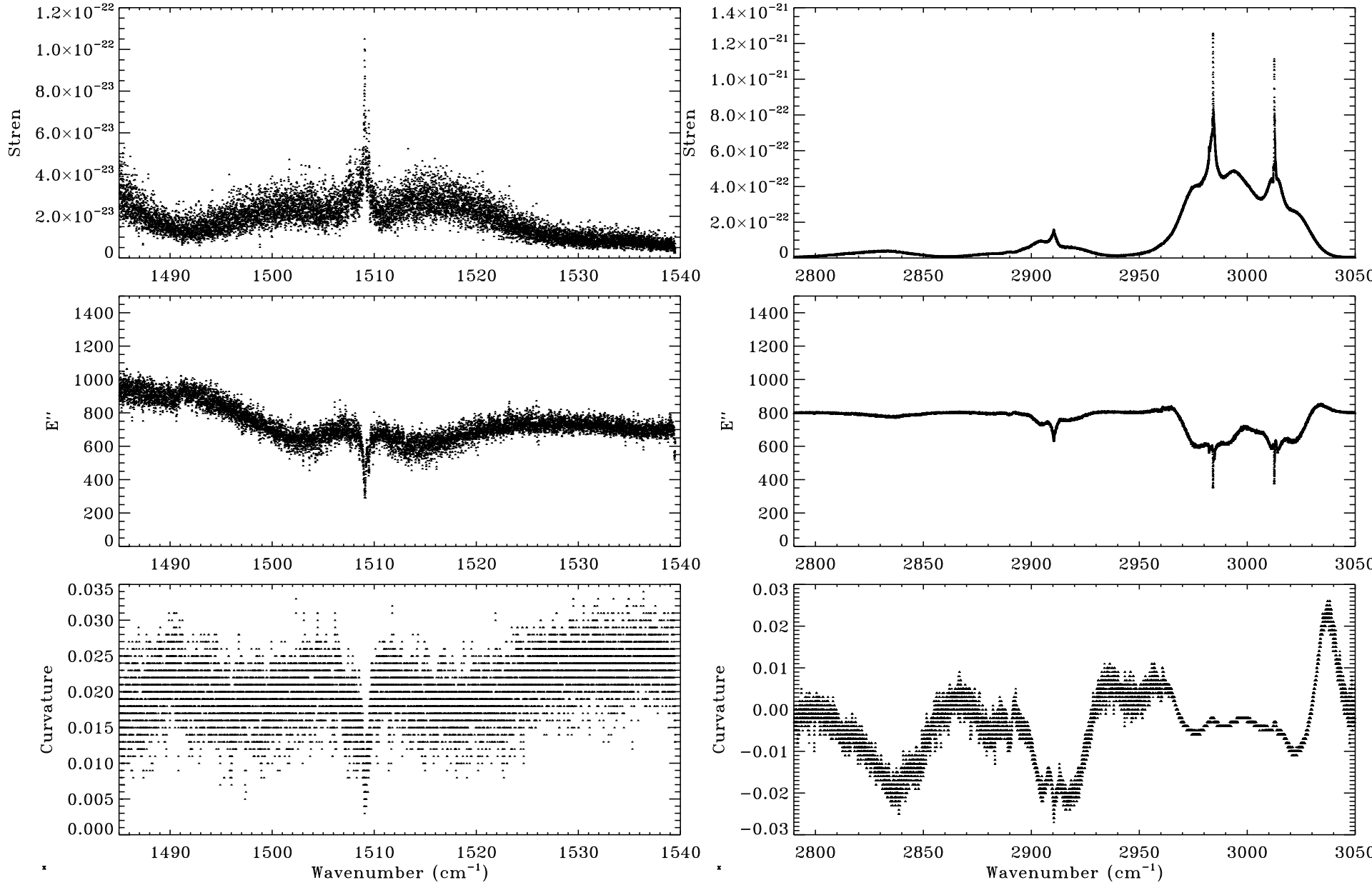
Properties of individual pseudo-lines