TEMPERATURE DEPENDENCE OF AIR-BROADENED HALF WIDTH AND PRESSURE SHIFT COEFFICIENTS IN THE 30012 - 00001 BAND OF $^{12}C^{16}O_2$

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The Orbiting Carbon Observatory requires high accuracy retrievals of carbon dioxide (~0.3%) in the 30012-00001 and 30013-00001 bands at 1.6 microns. Previously we have determined the positions, intensities, self and air broadened Lorentz halfwidths, self and air induced pressure shifts, line mixing and speed dependence at room temperature of the spectral lines in these bands from spectra acquired with the Kitt Peak FTS. The Bomem FTS at the National Research Council of Canada was used to obtain additional air broadened spectra at temperatures as low as ~215 K. The new multispectrum nonlinear least squares fits have fixed the self broadening, line mixing and speed dependence to those values determined in the previous study. This work describes the derivation of the temperature dependence of the air broadened halfwidth and air induced pressure shift. A single fit including the entire band and all 39 spectra was made for each band.

Summary of experimental conditions of the CO_2 spectra analyzed in this work

Pure CO_2				**CO_2 in air**			
Temp (K)	Pressure (torr)	Path (m)	CO_2 (VMR)	Temp (K)	Pressure (torr)	Path (cm)	CO_2 (VMR)
293.94	26.10[a]	24.94	1.0	258.9	370.4	40.15	0.101
294.05	11.04[a]	24.94	1.0	258.9	249.5	40.15	0.101
CO_2 in air				258.9	153.9	40.15	0.105
292.92	923.52	121.18	0.0593	258.9	77.8	40.15	0.106
293.07	250.38	121.18	0.0595				
292.79	100.86	121.18	0.0605	244.35	709.0	80.15	0.102
293.34	551.29	49.00	0.0152				
293.05	549.545	49.00	0.0499	234.40	600.2	60.15	0.102
293.17	200.25	49.00	0.0155	234.40	450.6	60.15	0.102
293.03	100.00	49.00	0.0160	234.40	299.9	60.15	0.102
293.17	50.07	49.00	0.0749	234.40	199.9	60.15	0.104
292.88	49.79	49.00	0.0160	234.40	100.3	60.15	0.104
292.63	26.05	49.00	0.0679	234.40	59.8	60.15	0.109
292.75	25.09	49.00	0.0170				
				219.00	749.0	80.15	0.102
296.00	798.0	80.15	0.102	219.00	601.0	80.15	0.102
296.00	501.0	80.15	0.102	219.00	450.5	80.15	0.102
295.20	100.5	80.15	0.1038	219.00	300.5	80.15	0.102
291.00	492.0	80.15	0.102				
				215.3	601.7	40.15	0.102
273.00	601.0	80.15	0.102	215.3	498.4	40.15	0.102
273.00	401.0	80.15	0.102	215.3	301.3	40.15	0.102
258.9	652.1	40.15	0.102				
258.9	500.8	40.15	0.103				

[a] Pure natural CO_2 samples (Volume Mixing Ratio = 1 with 0.9842 $^{16}O^{12}C^{16}O$)

1 atm = 101.3 kPa = 760 torr

Comparisons of line positions and intensities

(This Study vs. Literature Values)

Band	Line	Position (cm^{-1})		Intensity (cm $molecule^{-1}$) at 296 K	
		This Study	Literature Value	This Study	Literature Value
30013←00001[¥]	P24	6207.245780	6207.24563	1.2852e-23	1.2913e-23
	P20	6210.973788	6210.97364	1.5012e-23	1.5090e-23
	P10	6219.796860	6219.79671	1.3461e-23	1.3540e-23
	P2	6226.348831	6226.34868	3.2868e-24	3.3064e-24
	R10	6236.037128	6236.03698	1.5047e-23	1.5126e-23
	R20	6242.672293	6242.67214	1.6262e-23	1.6326e-23
	R26	6246.304618	6246.30455	1.2431e-23	1.2467e-23
30012←00001[§]	P24	6327.061058	6327.06089	1.2648e-23	1.2717e-23
	P20	6330.821403	6330.82124	1.4943e-23	1.5035e-23
	P10	6339.708766	6339.70860	1.3659e-23	1.3760e-23
	P2	6346.282680	6346.28251	3.3548e-24	3.3809e-24
	R10	6355.938961	6355.93880	1.5231e-23	1.5342e-23
	R20	6362.503955	6362.50379	1.6116e-23	1.6211e-23
	R26	6366.087194	6366.08703	1.2089e-23	1.2146e-23

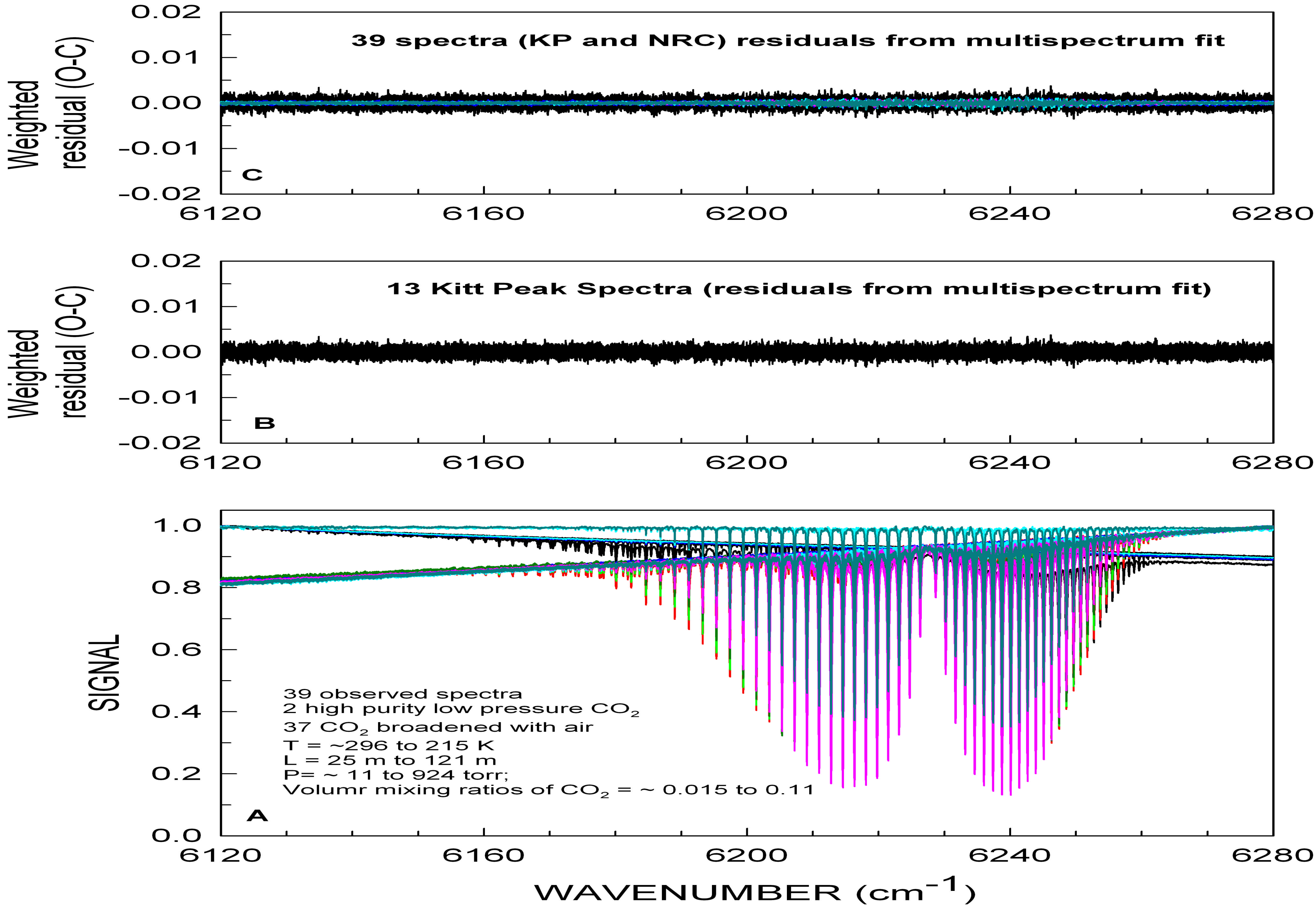
Lines positions between this study and literature values agree to within 0.0002 cm^{-1}.

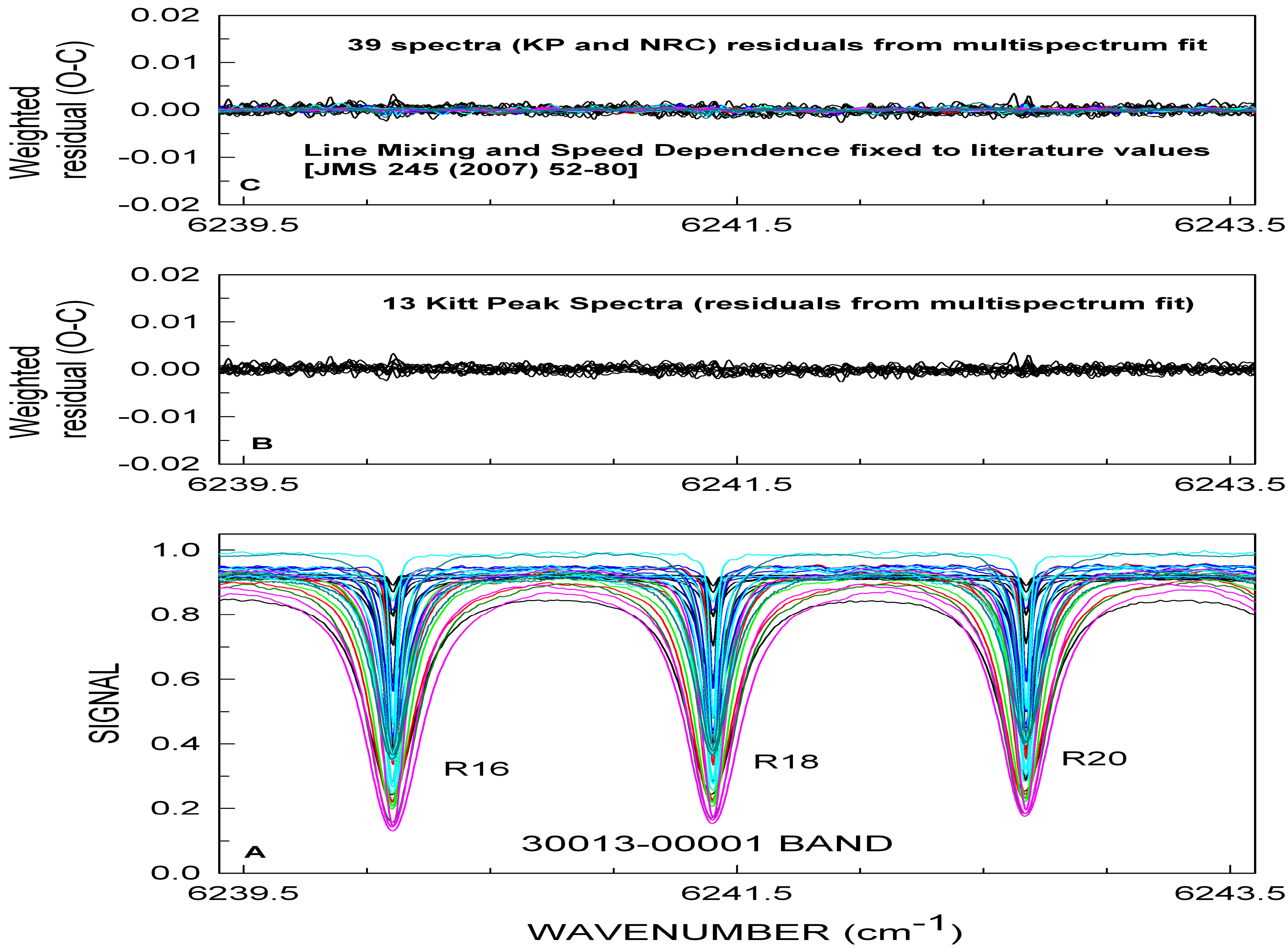
Line intensities between the two datasets agree within ~0.5%.

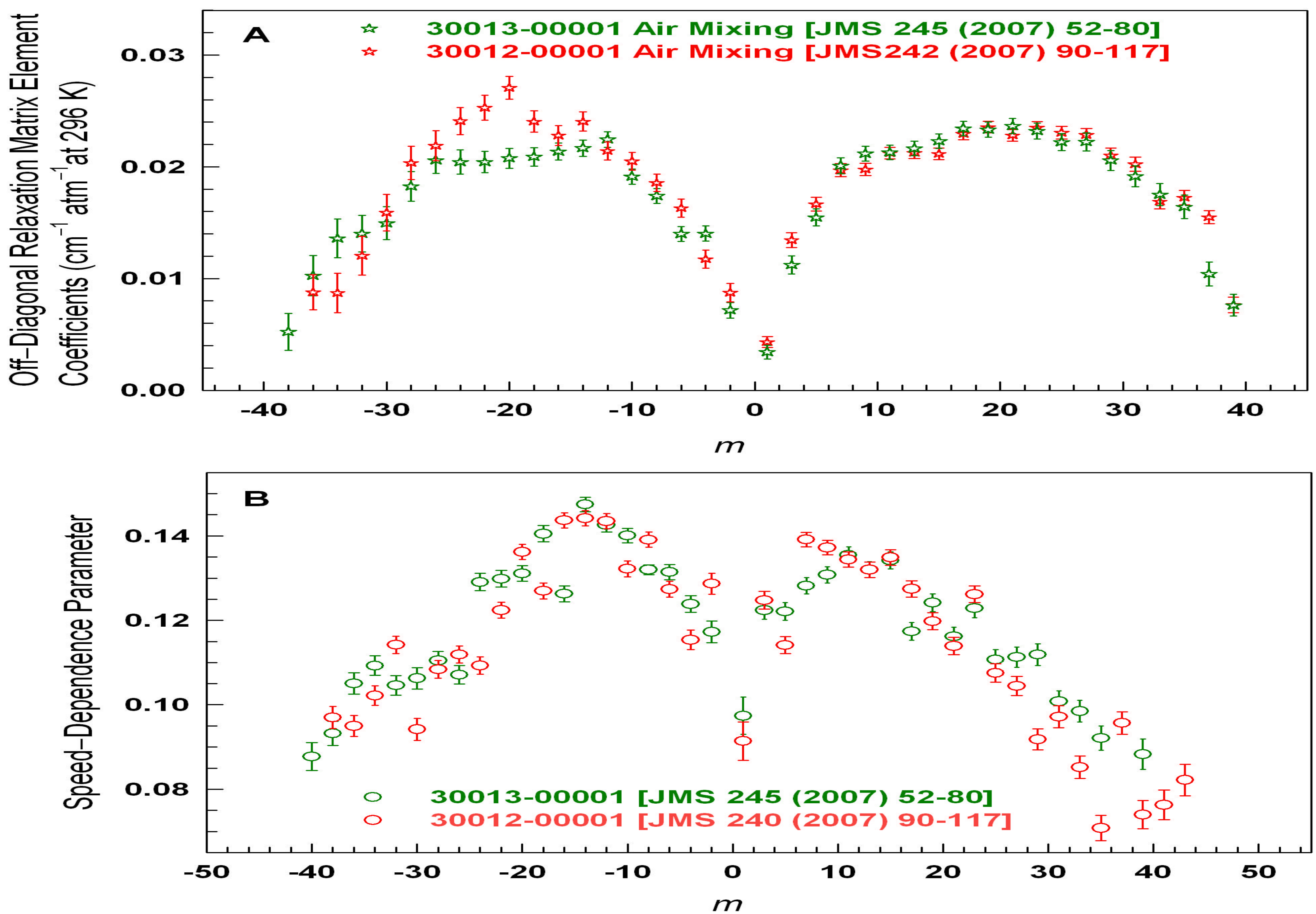
¥ JMS 245 (2007) 52-80.

§ JMS 242 (2007) 90-117

Color codes for spectra plotted:
Black: Room temperature Kitt Peak Spectra
Red: 296 K spectra from NRC
Light Green: 274 K spectra from NRC
Blue: 259 K spectra from NRC
Dark Green: 244 K spectra from NRC
Cyan: 234 K spectra from NRC
Pink: 219 K spectra from NRC
Dark Cyan: 215 K spectra from NRC


39 spectra (KP and NRC) residuals from multispectrum fit
Weighted residual (O-C)
0.02
0.01
0.00
-0.01
-0.02
C
6120
6160
6200
6240
6280
13 Kitt Peak Spectra (residuals from multispectrum fit)
Weighted residual (O-C)
0.02
0.01
0.00
-0.01
-0.02
B
6120
6160
6200
6240
6280
SIGNAL
1.0
0.8
0.6
0.4
0.2
0.0
39 observed spectra
2 high purity low pressure CO2
37 CO2 broadened with air
T = ~296 to 215 K
L = 25 m to 121 m
P= ~ 11 to 924 torr;
Volumr mixing ratios of CO2 = ~ 0.015 to 0.11
A
6120
6160
6200
6240
6280
WAVENUMBER (cm-1)


39 spectra (KP and NRC) residuals from multispectrum fit
Line Mixing and Speed Dependence fixed to literature values
[JMS 245 (2007) 52-80]
C
Weighted residual (O-C)
0.02
0.01
0.00
-0.01
-0.02
6239.5
6241.5
6243.5
13 Kitt Peak Spectra (residuals from multispectrum fit)
B
Weighted residual (O-C)
0.02
0.01
0.00
-0.01
-0.02
6239.5
6241.5
6243.5
SIGNAL
1.0
0.8
0.6
0.4
0.2
0.0
R16
R18
R20
A
30013-00001 BAND
6239.5
6241.5
6243.5
WAVENUMBER (cm-1)


A
30013-00001 Air Mixing [JMS 245 (2007) 52-80]
30012-00001 Air Mixing [JMS242 (2007) 90-117]
Off–Diagonal Relaxation Matrix Element
Coefficients (cm⁻¹ atm⁻¹ at 296 K)
0.00
0.01
0.02
0.03
-40
-30
-20
-10
0
10
20
30
40
m
B
30013-00001 [JMS 245 (2007) 52-80]
30012-00001 [JMS 240 (2007) 90-117]
Speed–Dependence Parameter
0.08
0.10
0.12
0.14
-50
-40
-30
-20
-10
0
10
20
30
40
50
m

Rather than solve for the positions and intensities of the individual spectral lines, the multispectrum nonlinear least squares fit solved for the G', B', D', H', band strength and up to two Herman Wallis coefficients for each band. These figures show the sensitivity of each point in each spectrum to each of these parameters for the 30013-00001 band.

Equations used for position constraints

$$\nu_i = G' - G'' + (B'J'[J'+1] - D'\{J'[J'+1]\}^2 + H'\{J'[J'+1]\}^3)$$
$$- (B''J''[J''+1] - D''\{J''[J''+1]\}^2 + H''\{J''[J''+1]\}^3) \qquad (1)$$

Equations used for Band Intensity parameters

$$S_i = \frac{S_\nu \nu_i L_i F}{Q_r \nu_0} \exp\left(\frac{-C_2 E''}{T_0}\right)\left[1 - \exp\left(\frac{-C_2 \nu_i}{T_0}\right)\right]$$

where,

$$F = (1 + a_1 m + a_2 m^2 + a_3 m^3 + a_4 J(J+1))^2$$

ν_i denotes the wavenumber (cm^{-1}) of the i^{th} transition, and prime and double prime denote the upper and lower vibrational levels, respectively. In Eq. 2, L_i are the Hönl-London factors, C_2 represents the second radiation constant and other terms have their usual significance. The terms a_1 and a_2 in Eq. (3) were sufficient to describe the bands to the noise level of the spectra once the speed dependence and line mixing were utilized.

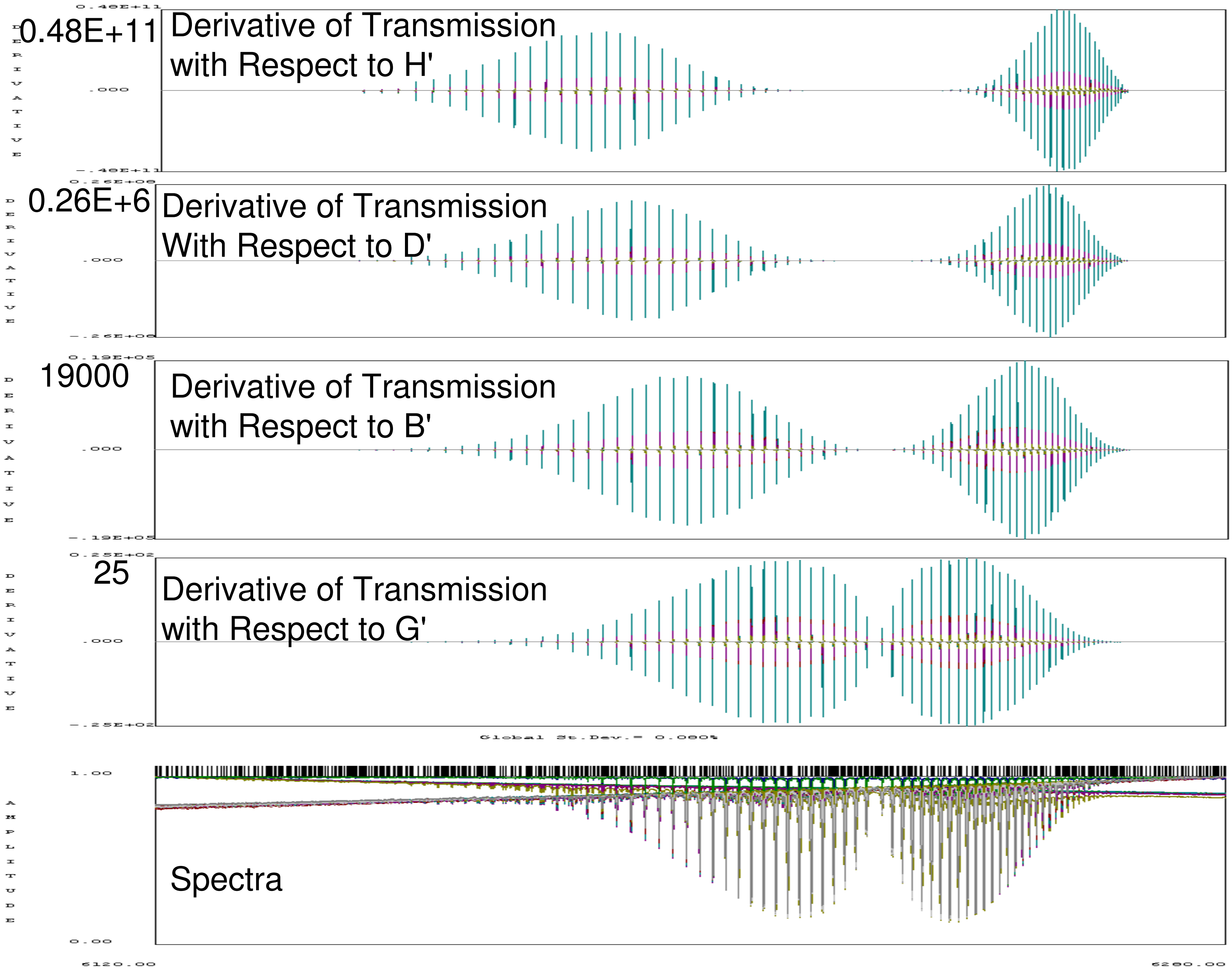
Temperature dependences of pressure-broadened width and shift coefficients were determined using the Eqs. given below:

$$b_L(p,T) = p\left[b_L^0(air)(p_0,T_0)(1-\chi)\left[\frac{T_0}{T}\right]^{n1} + b_L^0(self)(p_0,T_0)\chi\left[\frac{T_0}{T}\right]^{n2}\right] \qquad (4)$$

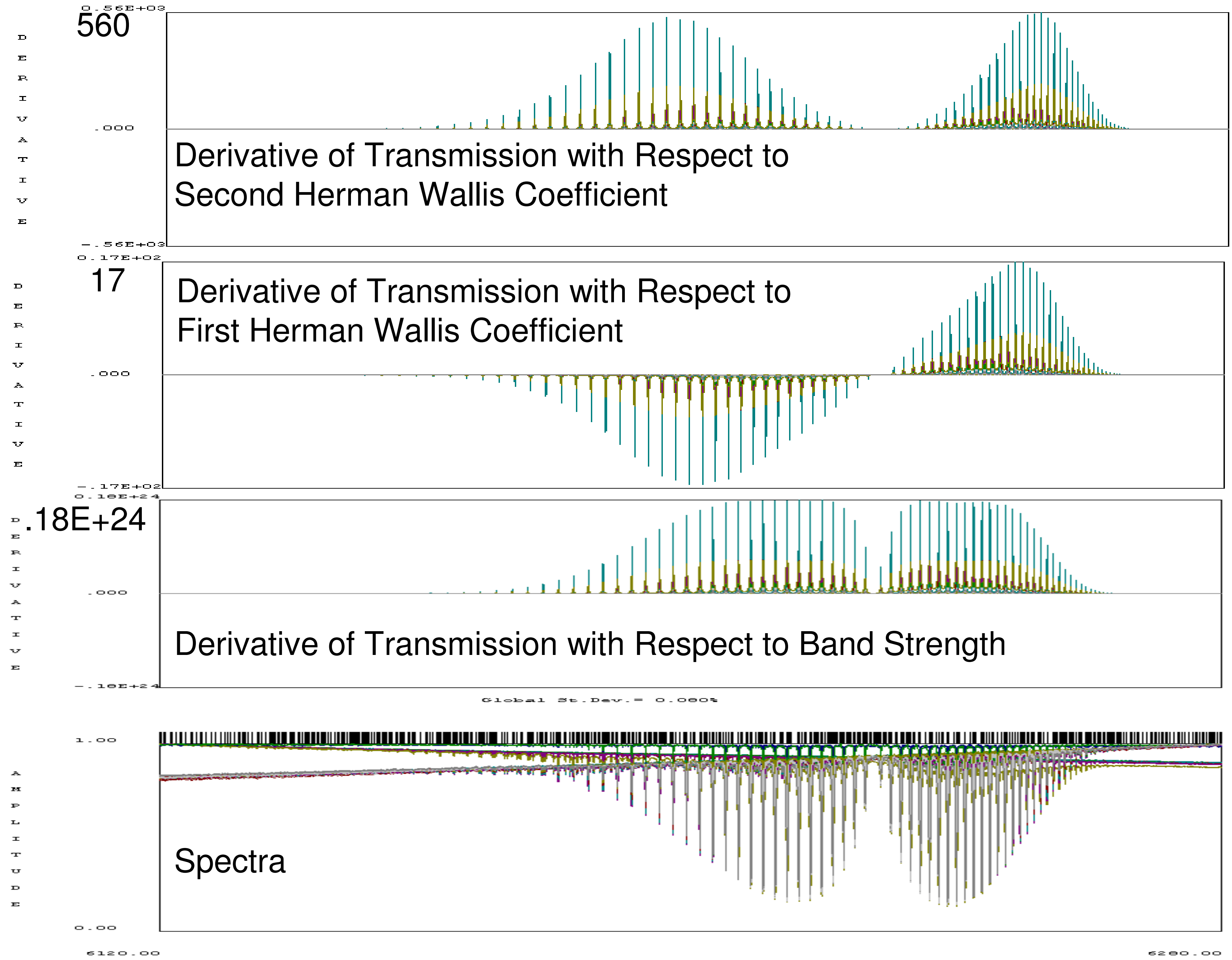
$$\nu = \nu_0 + p\left[\delta^0(air)(1-\chi) + \delta^0(self)\chi\right] \qquad (5)$$

$$\delta^0(T) = \delta^0(T_0) + \delta'(T - T_0) \qquad (6)$$

In Eqs. (4) – (6) b_L^0 and δ^0 represent pressure broadening and pressure shift coefficients (in cm^{-1} atm^{-1} at 296 K), respectively. b_L (p, T) is the Lorentz halfwidth (in cm^{-1}) of the spectral line at pressure p and temperature T, and $b_L^0(Gas)(p_0, T_0)$ is the Lorentz halfwidth coefficient of the line at the reference pressure p_0 (1 atm) and temperature T_0 (296 K) of the broadening gas (either air or CO_2), and χ is the ratio of the partial pressure of CO_2 to the total sample pressure in the cell. The temperature dependent exponents of air-broadened widths are n_1 and the temperature dependent coefficient of air-induced shift is δ'.



0.48E+11
Derivative of Transmission
with Respect to H'
0.26E+6
Derivative of Transmission
With Respect to D'
19000
Derivative of Transmission
with Respect to B'
25
Derivative of Transmission
with Respect to G'
Global St.Dev.= 0.080%
Spectra
AMPLITUDE
1.00
0.00
6120.00
6280.00
WAVENUMBER


560
0.56E+03
.000
-.56E+03
Derivative of Transmission with Respect to
Second Herman Wallis Coefficient
DERIVATIVE
17
0.17E+02
.000
-.17E+02
Derivative of Transmission with Respect to
First Herman Wallis Coefficient
DERIVATIVE
.18E+24
0.18E+24
.000
-.18E+24
Derivative of Transmission with Respect to Band Strength
DERIVATIVE
Global St.Dev.= 0.080%
1.00
0.00
AMPLITUDE
Spectra
6120.00
6280.00
WAVENUMBER

Rotational Constants: Comparison with literature values
30013←00001 and 30012←00001 bands of $^{12}C^{16}O_2$ [¥,§]

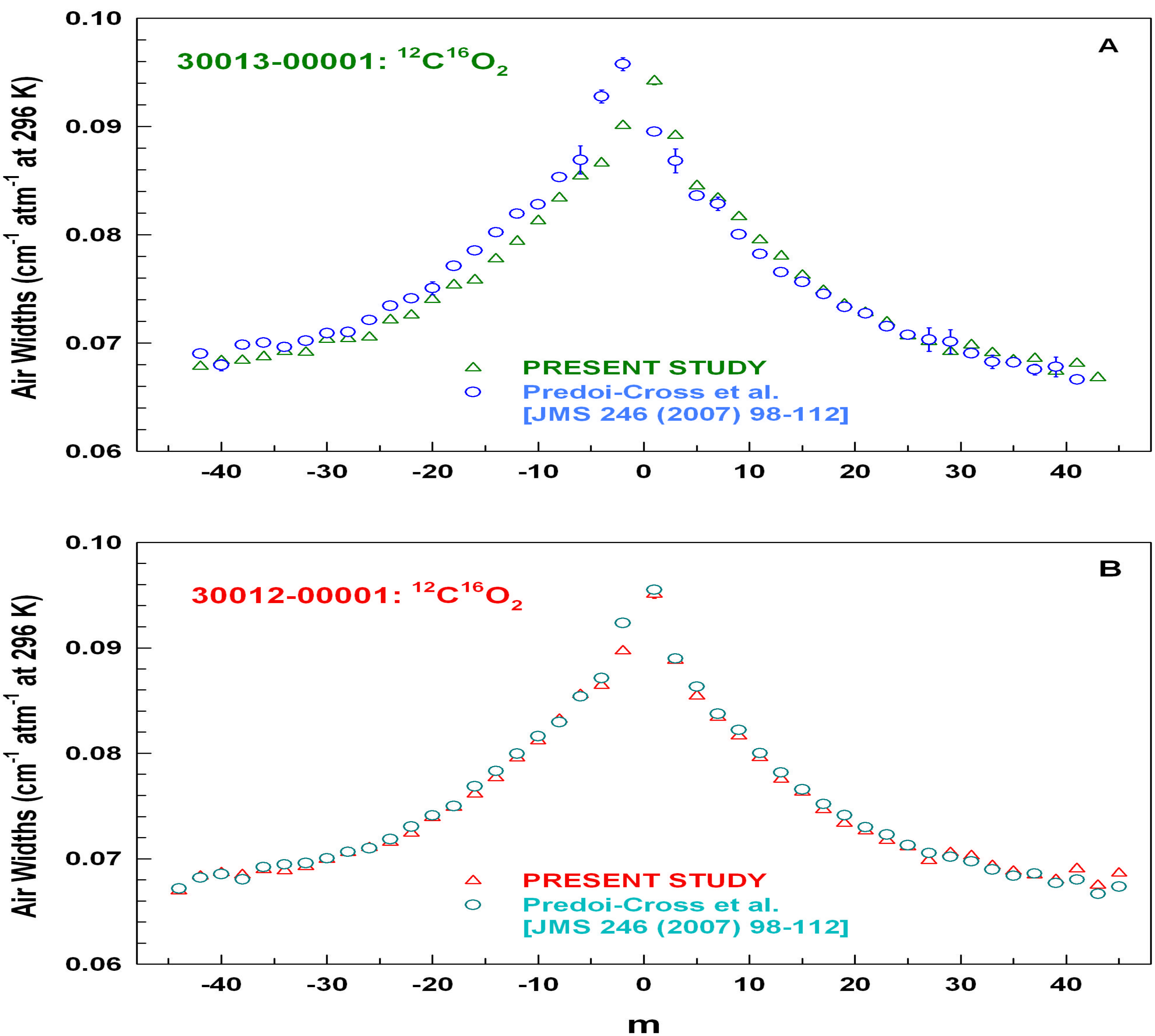
Rotational Constants	*30013←00001*		*30012←00001*	
	This Study	Literature Value[¥]	This Study	Literature Value[§]
G′	6227.916 718(6)	6227.916 565(4)	6347.851 079(6)	6347.850 911(4)
B′	0.386 711 133(24)	0.386 711 147(14)	0.386 455 026 (27)	0.386 455 070(15)
$D' \cdot 10^7$	1.716 882 (278)	1.717 038 (144)	0.982 766 (332)	0.983 477 (159)
$H' \cdot 10^{12}$	10.496 (86)	10.552 (38)	0.574 6(107)	0.597 4(44)

[¥]JMS 245 (2007) 52-80.
[§]JMS 242 (2007) 90-117.
Difference (G′): 30013←00001 (This study-Literature[¥]) = 0.000 16 cm^{-1}.
Difference (G′): 30012←00001 (This study-Literature[§]) = 0.000 17 cm^{-1}.

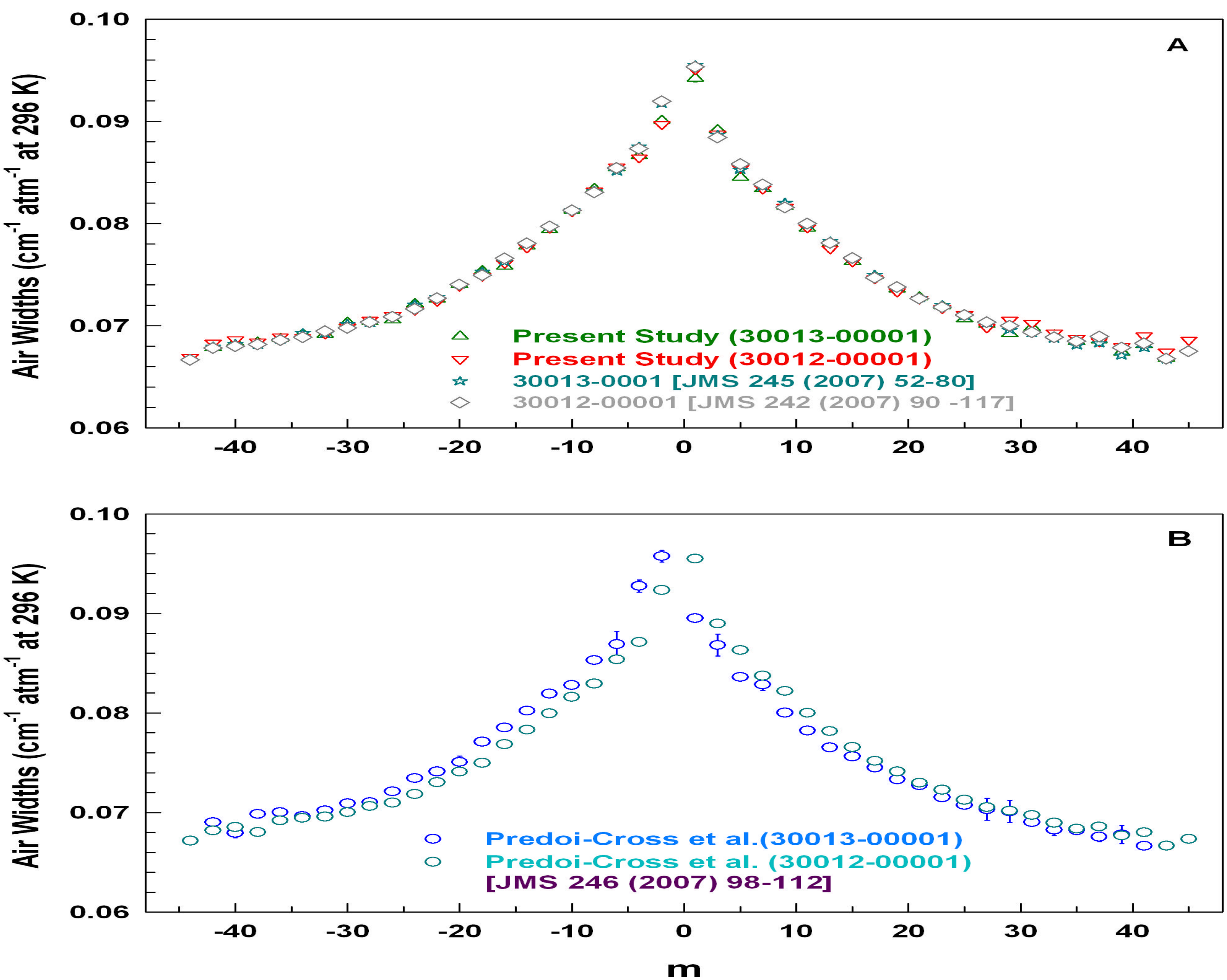
Band Intensity parameters: Comparison with literature values
30013←00001 and 30012←00001 bands of $^{12}C^{16}O_2$ [¥,§]

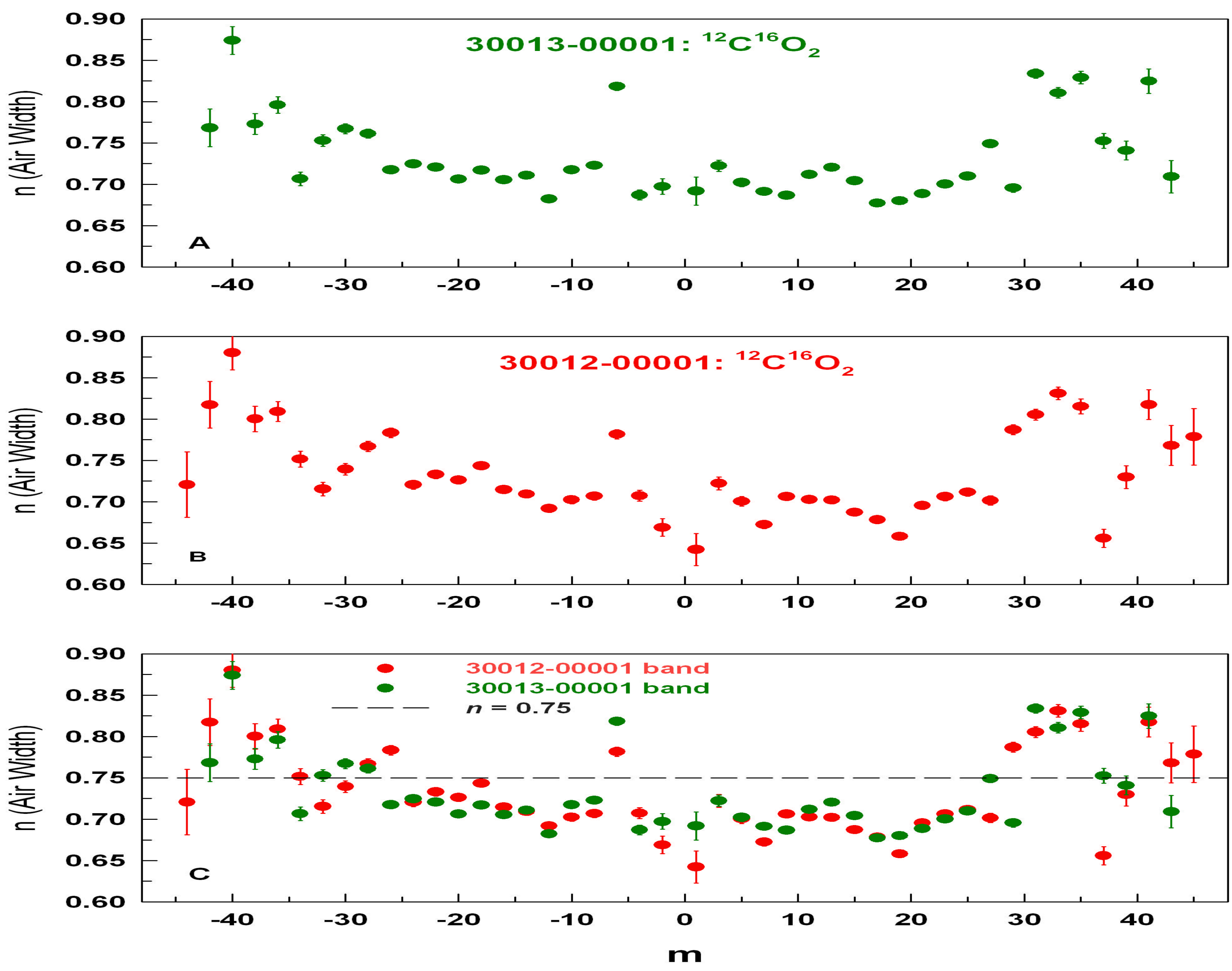
Intensity Parameter	*30013←00001*		*30012←00001*	
	This Study	Literature Value[¥]	This Study	Literature Value[§]
$Sv/Qr \cdot 10^{25}$	16.643 8 (16)	16.742 4 (20)	16.990 9 (20)	17.123 8 (24)
$A_1 \cdot 10^4$	3.018 (16)	2.880 (11)	2.775 (18)	2.762 (11)
$A_2 \cdot 10^5$	1.871 1(80)	1.710 6(44)	-1.395 3 (94)	-1.603 2(44)

[¥]JMS 245 (2007) 52-80.
[§]JMS 242 (2007) 90-117.

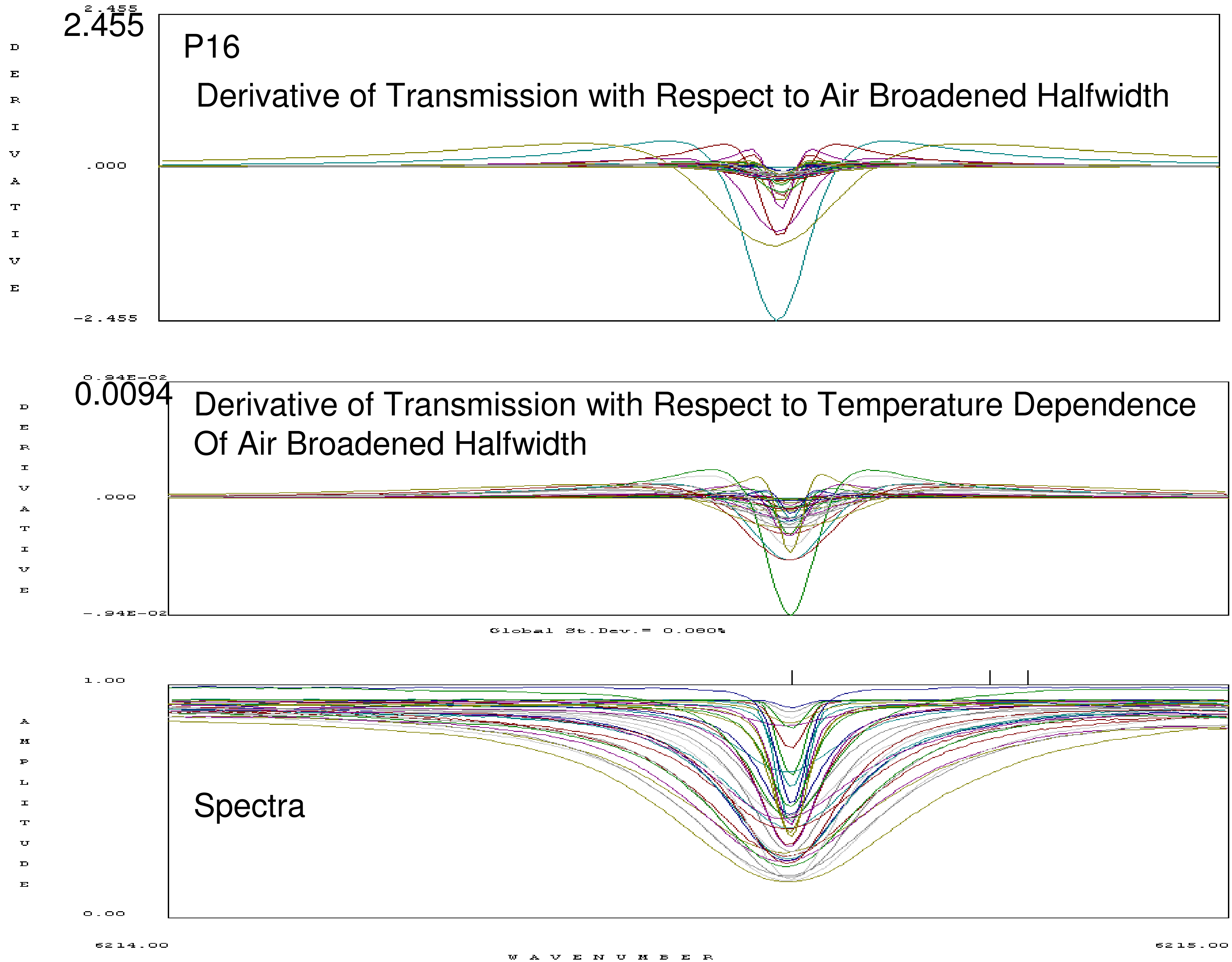


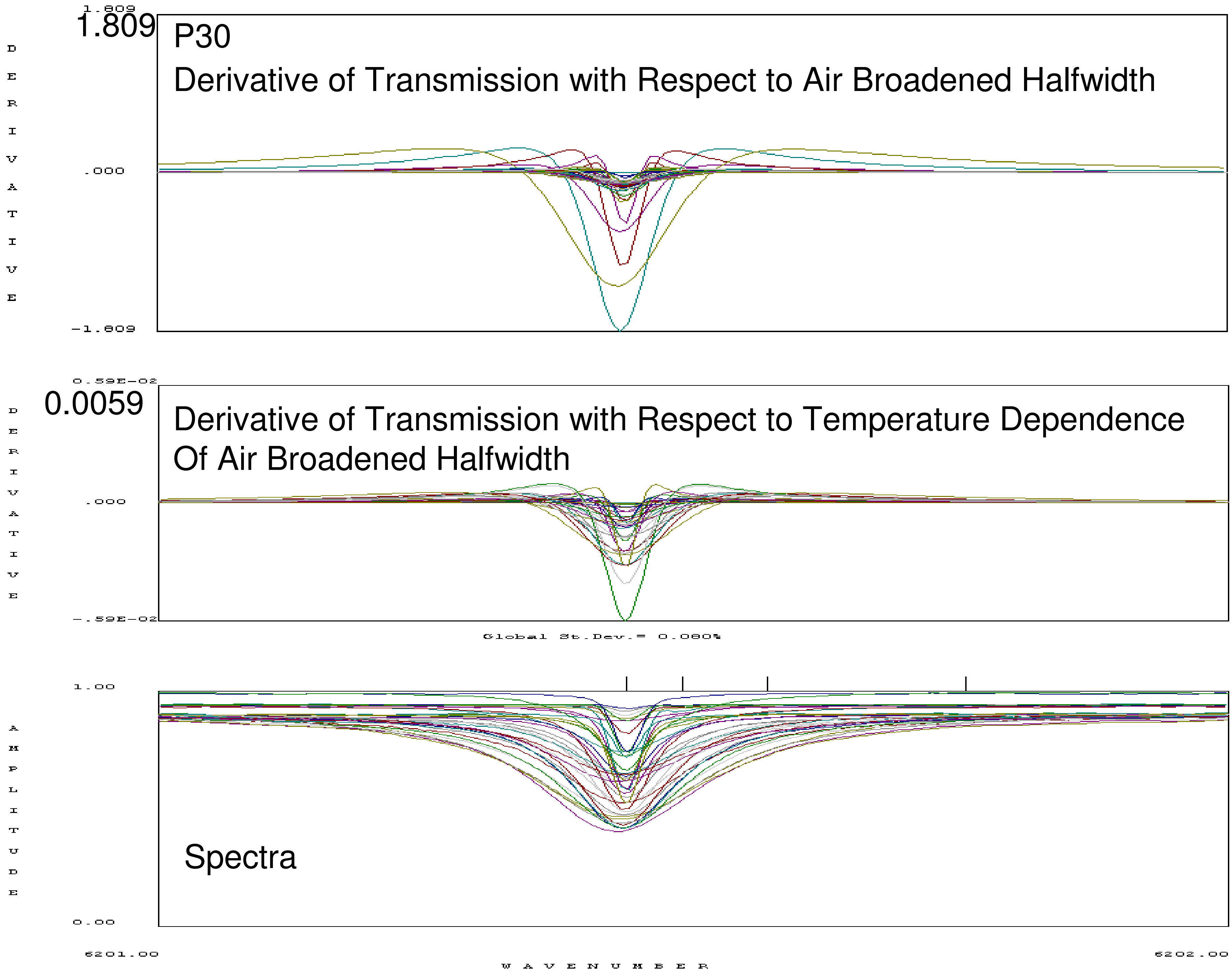
30013-00001: $^{12}C^{16}O_2$
A
PRESENT STUDY
Predoi-Cross et al.
[JMS 246 (2007) 98-112]
Air Widths (cm^{-1} atm^{-1} at 296 K)
0.10
0.09
0.08
0.07
0.06
-40
-30
-20
-10
0
10
20
30
40
30012-00001: $^{12}C^{16}O_2$
B
PRESENT STUDY
Predoi-Cross et al.
[JMS 246 (2007) 98-112]
m

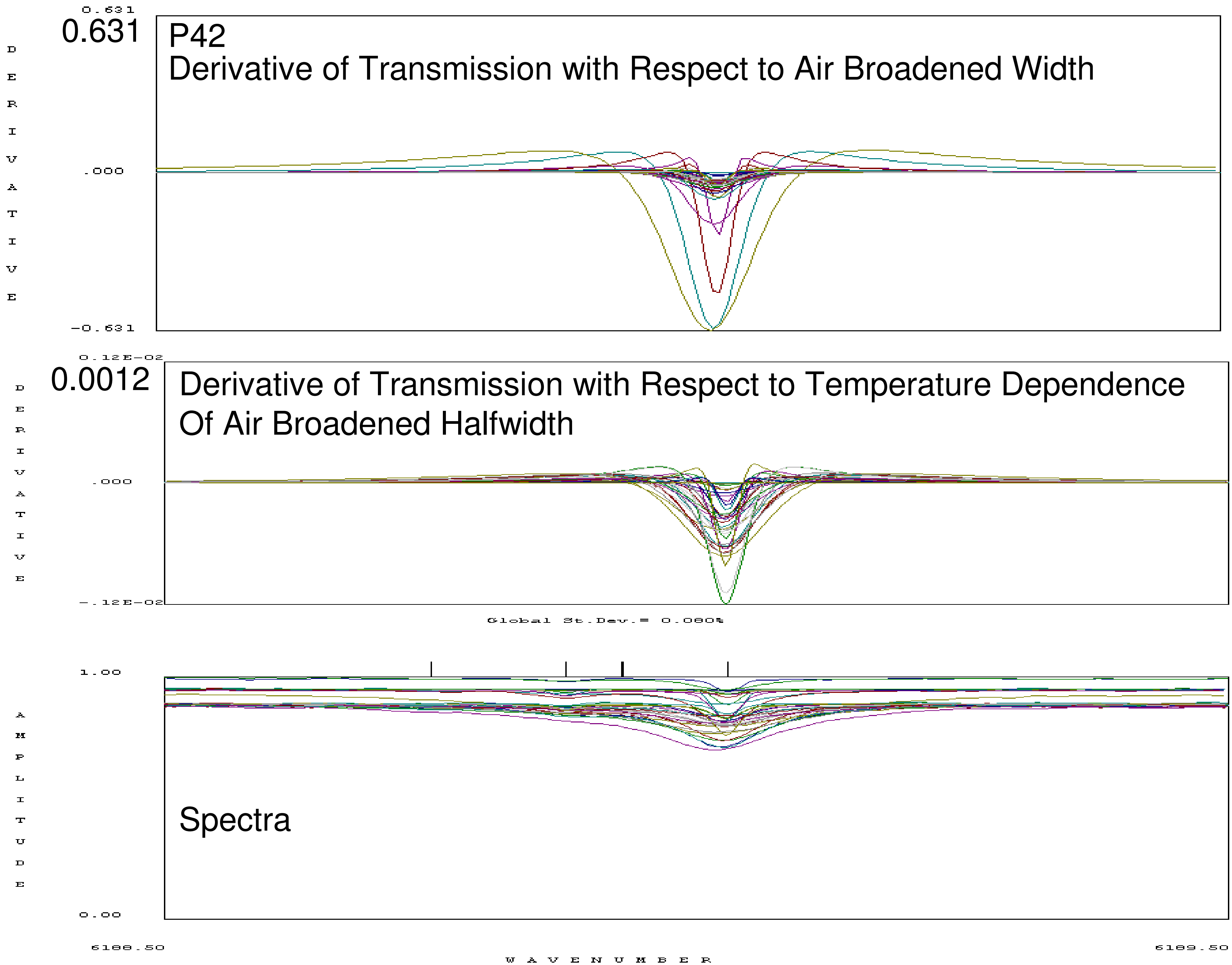

A
Present Study (30013-00001)
Present Study (30012-00001)
30013-0001 [JMS 245 (2007) 52-80]
30012-00001 [JMS 242 (2007) 90 -117]
B
Predoi-Cross et al.(30013-00001)
Predoi-Cross et al. (30012-00001)
[JMS 246 (2007) 98-112]
Air Widths (cm-1 atm-1 at 296 K)
m


30013-00001: $^{12}C^{16}O_2$
A
30012-00001: $^{12}C^{16}O_2$
B
C
30012-00001 band
30013-00001 band
n = 0.75
n (Air Width)
m

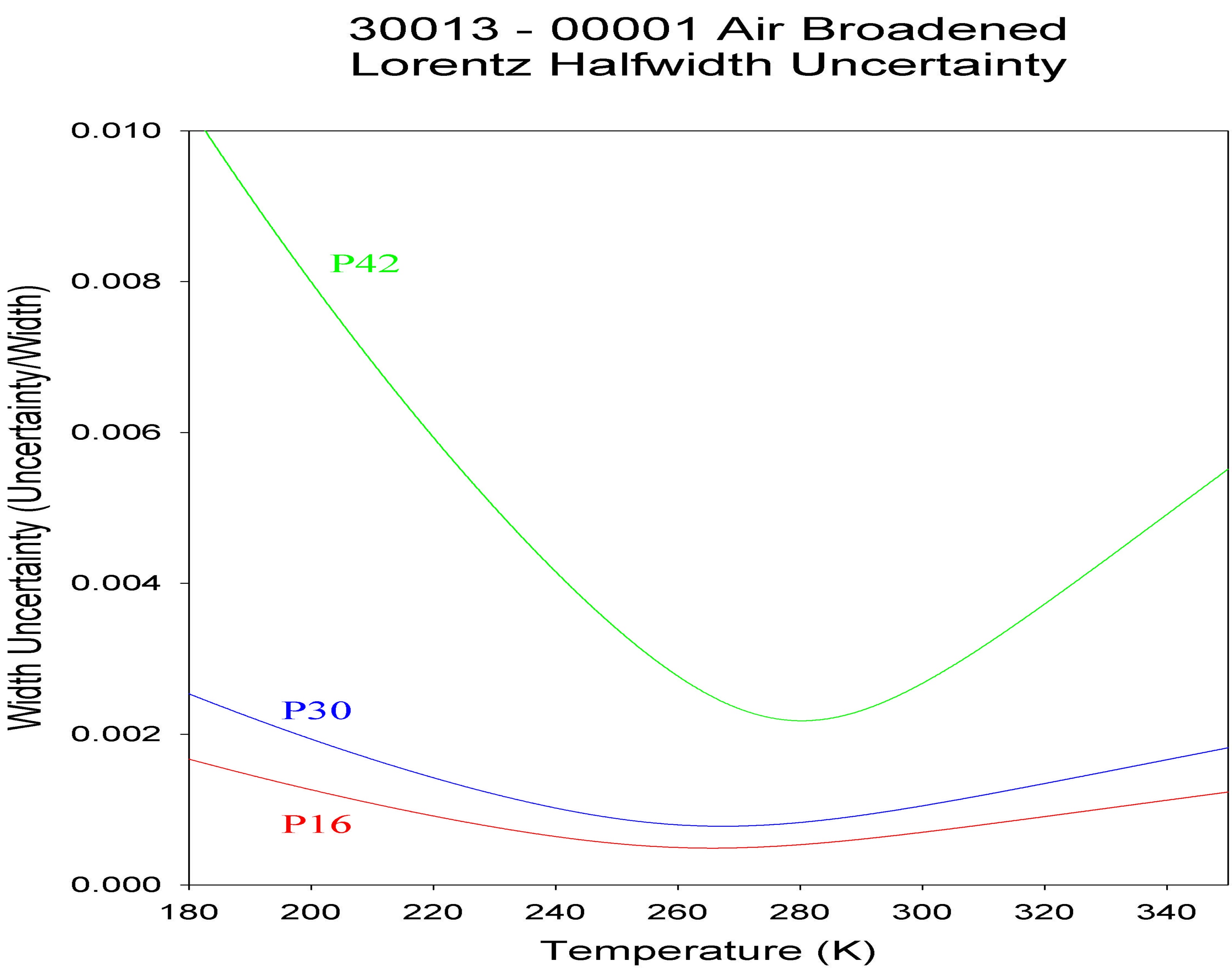
These three figures display the sensitivity of each spectral point near the appropriate spectral line on each spectrum to the Lorentz air broadened halfwidth and its temperature dependence. The lines displayed are the P16, P30 and P42 lines of the 30013-00001 band. The temperature dependence exponent sensitivity lies primarily in different spectra than that of the halfwidth at 296 K. The higher J lines have less sensitivity than the lower J lines and the P42 line shows a different pattern of spectra which provide most of the information. The P42 line is very weak in the low temperature spectra and the temperature dependence is determined more poorly.

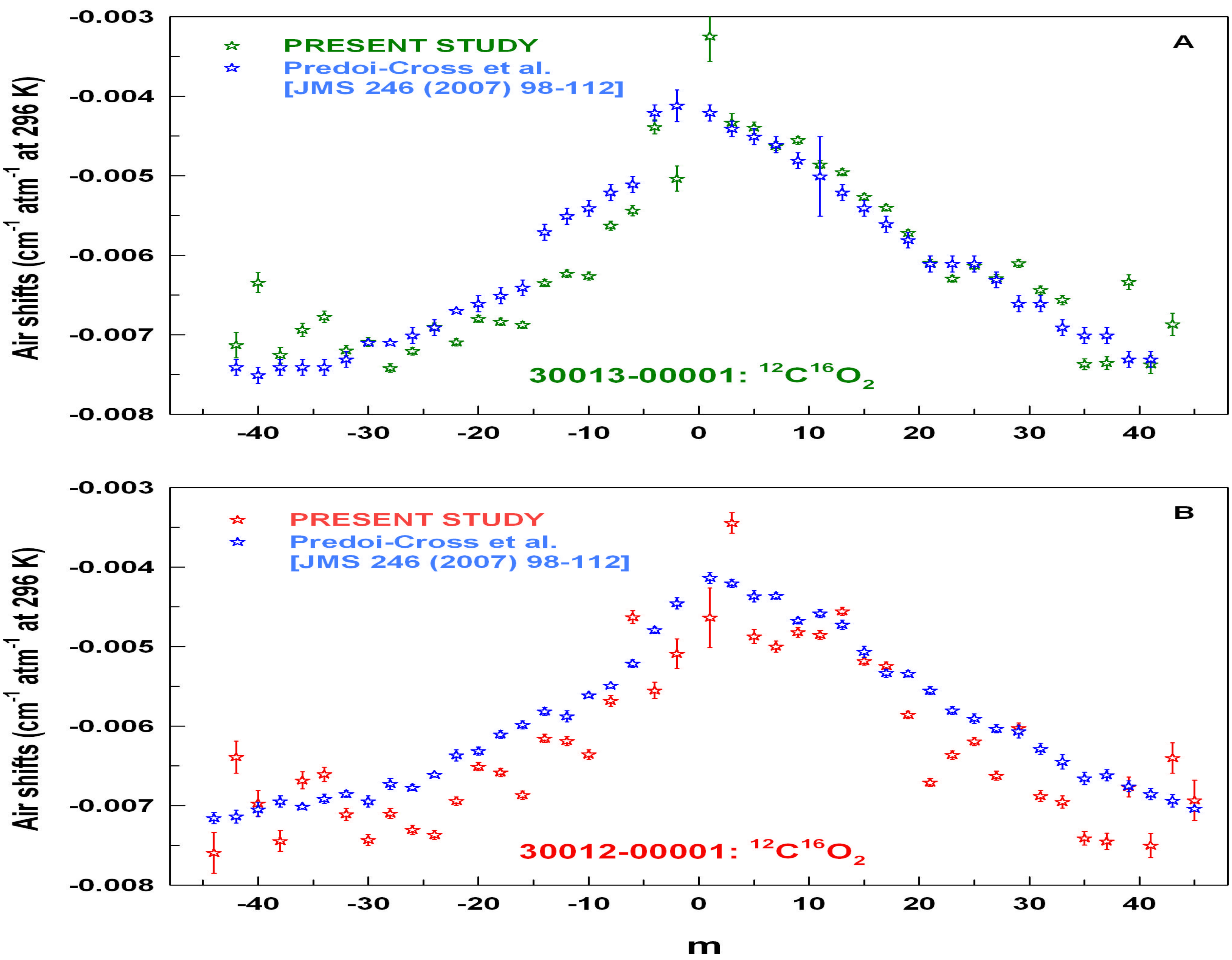

P16
Derivative of Transmission with Respect to Air Broadened Halfwidth
2.455
.000
-2.455
DERIVATIVE
Derivative of Transmission with Respect to Temperature Dependence Of Air Broadened Halfwidth
0.0094
0.94E-02
.000
-.94E-02
DERIVATIVE
Global St.Dev.= 0.080%
Spectra
1.00
0.00
AMPLITUDE
6214.00
6215.00
WAVENUMBER

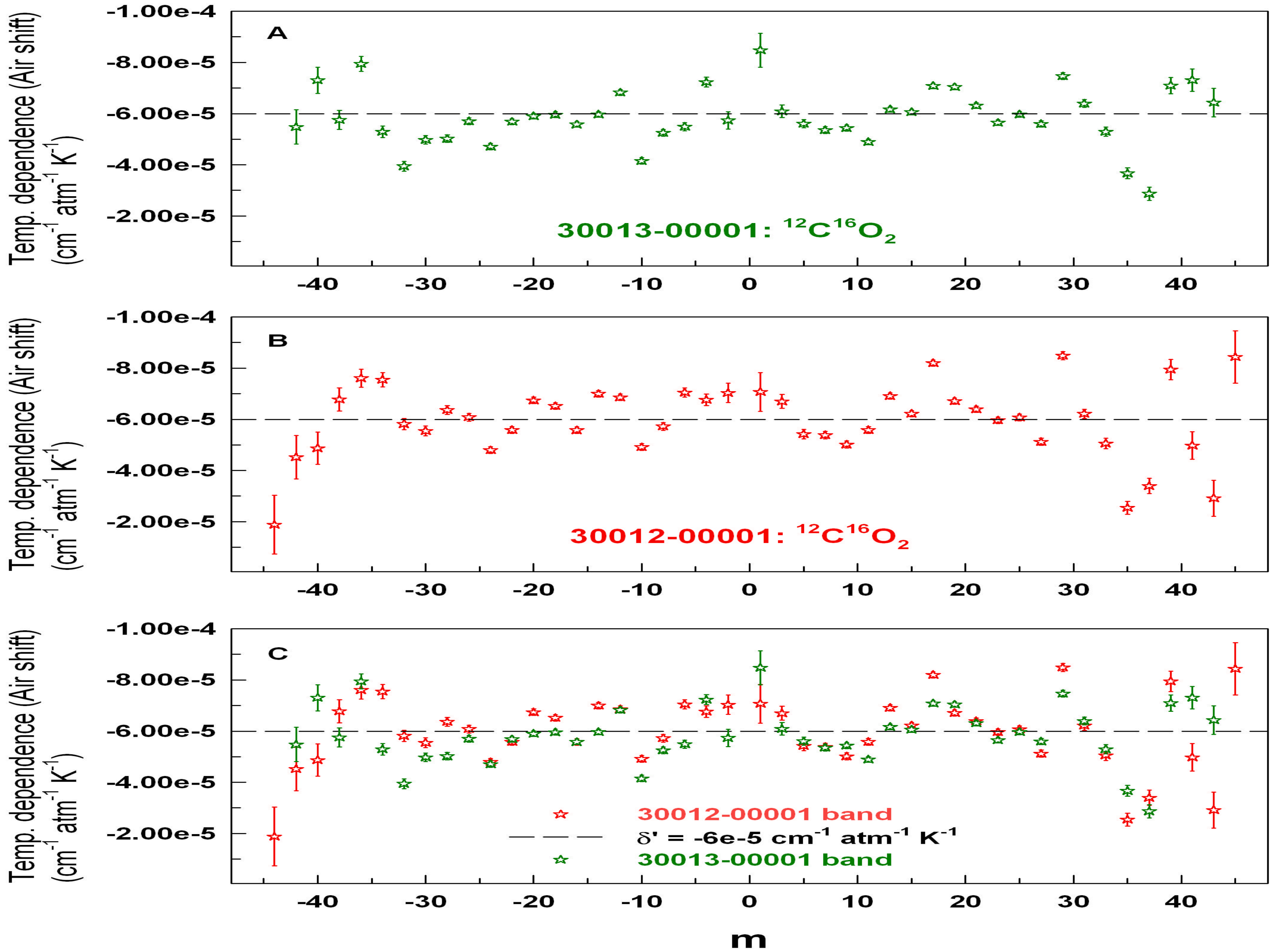

1.809
P30
Derivative of Transmission with Respect to Air Broadened Halfwidth
DERIVATIVE
1.809
.000
-1.809
0.0059
Derivative of Transmission with Respect to Temperature Dependence
Of Air Broadened Halfwidth
DERIVATIVE
0.59E-02
.000
-.59E-02
Global St.Dev.= 0.080%
Spectra
AMPLITUDE
1.00
0.00
6201.00
6202.00
WAVENUMBER


P42
Derivative of Transmission with Respect to Air Broadened Width
0.631
0.631
.000
-0.631
DERIVATIVE
Derivative of Transmission with Respect to Temperature Dependence Of Air Broadened Halfwidth
0.0012
0.12E-02
.000
-.12E-02
DERIVATIVE
Global St.Dev.= 0.080%
Spectra
1.00
0.00
AMPLITUDE
6188.50
6189.50
WAVENUMBER

The derived halfwidth and its temperature dependence are highly anticorrelated (~ -0.7) in the fit. While the HITRAN gives an uncertainty in the air broadened Lorentz halfwidth at 296 K along with an uncertainty and its temperature dependence exponent along with an uncertainty, one cannot derive the uncertainty of the halfwidth at another temperature without the correlation coefficient. This figure displays the actual uncertainty as a function of temperature for the air broadened Lorentz halfwidth of the P16, P30 and P42 lines of the 30013-00001 band of $^{12}C^{16}O_2$ from this study. The uncertainties of the P16 and P30 lines are nearly constant and smallest over the range of temperatures of the spectra in the fit. The P42 line has larger uncertainties due to its weaker intensity and it is not well constrained at low temperatures since the Boltzman statistics leave few molecules in its lower state. While the internal uncertainties are very small, the actual uncertainties are often dominated by the systematic experimental uncertainties at the level of about 0.5%.


30013 - 00001 Air Broadened
Lorentz Halfwidth Uncertainty
Width Uncertainty (Uncertainty/Width)
0.010
0.008
0.006
0.004
0.002
0.000
180
200
220
240
260
280
300
320
340
Temperature (K)
P42
P30
P16


A
PRESENT STUDY
Predoi-Cross et al.
[JMS 246 (2007) 98-112]
30013-00001: $^{12}C^{16}O_2$
B
PRESENT STUDY
Predoi-Cross et al.
[JMS 246 (2007) 98-112]
30012-00001: $^{12}C^{16}O_2$
Air shifts (cm^{-1} atm^{-1} at 296 K)
m


A
B
C
30013-00001: $^{12}C^{16}O_2$
30012-00001: $^{12}C^{16}O_2$
30012-00001 band
δ' = -6e-5 cm^{-1} atm^{-1} K^{-1}
30013-00001 band
Temp. dependence (Air shift) (cm^{-1} atm^{-1} K^{-1})
-1.00e-4
-8.00e-5
-6.00e-5
-4.00e-5
-2.00e-5
-40
-30
-20
-10
0
10
20
30
40
m