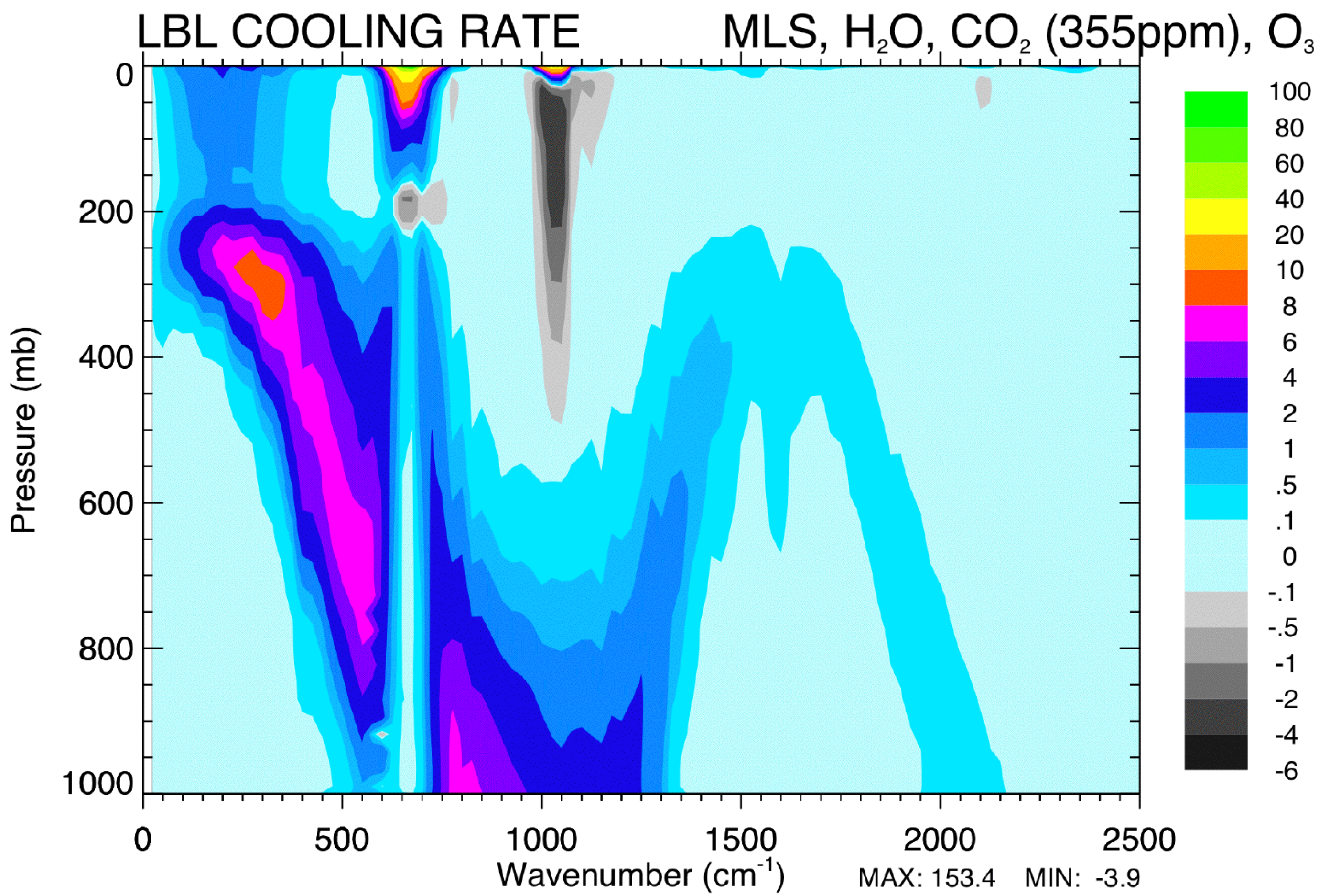
CRA

Forward Modeling for Far-Infrared Remote Sensing: Spectroscopic Issues and Line-by-Line Modeling

Tony Clough

Clough Radiation Associates, LLC

and a host of colleagues



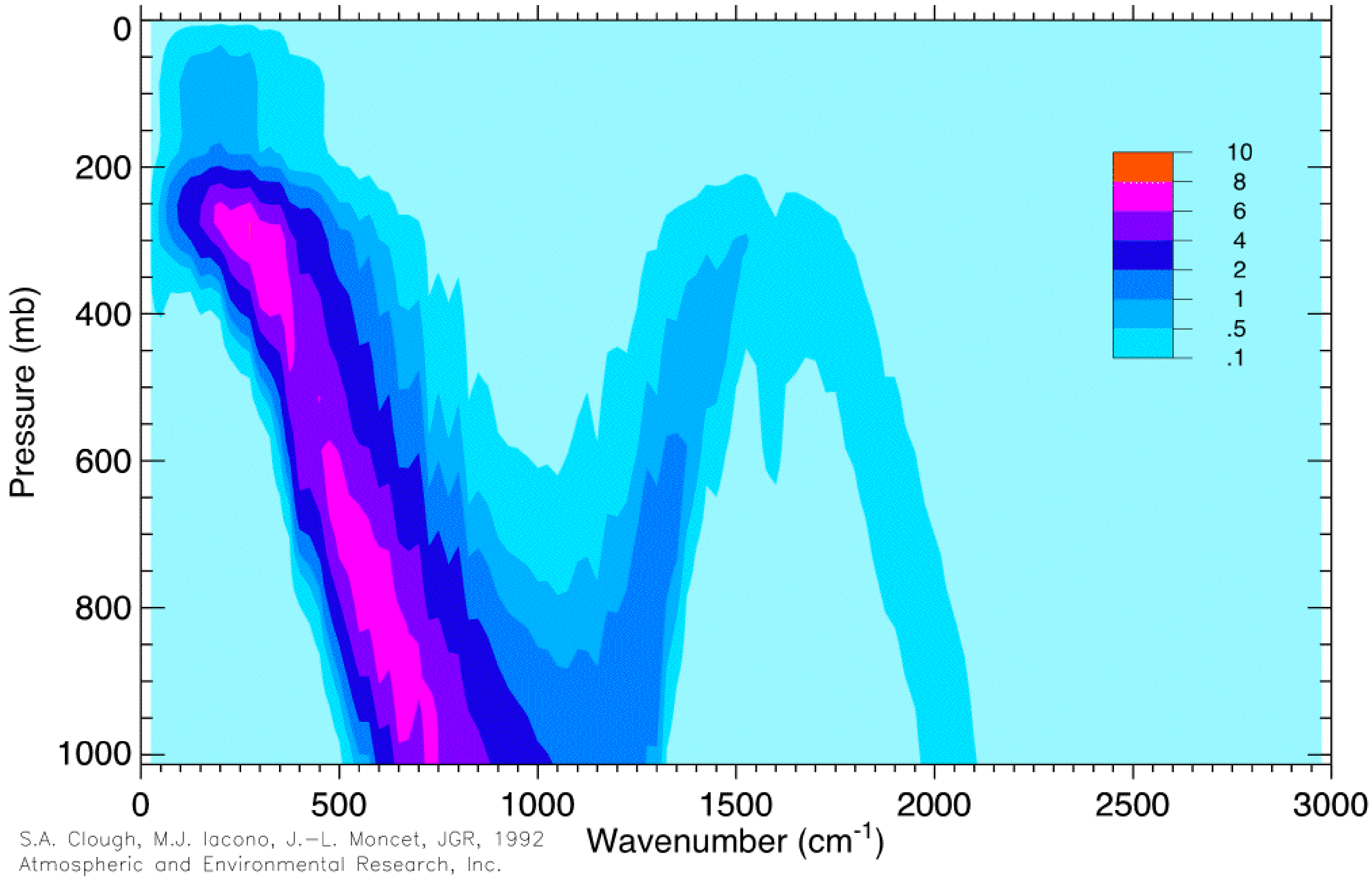
Shepard A. Clough, and Michael J. Iacono, JGR, 1995.
Atmospheric and Environmental Research, Inc.

Scale: x10^{-3} K/(day cm^{-1})

Contribution of the atmosphere to the outgoing spectral radiance

MLS Summer

Color scale x 10-7 is in units of W (cm2 sr cm-1)-1.



Formalism for the Spectral Calculation of Absorption I

- Validity from Microwave through Solar UV
- Detail Balance across entire extent of the line
  - **Radiance = Planck_Fn * [1 - Transmittance]**

A Bit of History: With a nod to the heroes of the profession!

Problem: (~1972)
Incoherent understanding of line shape associated with binary collisions
What is the validity of the impact line shape ?
What is the line shape far from line center that satisfies the physical constraints?

Harvard

Van Vleck

- Phillip Anderson thesis (student of Van Vleck) (ATC) (1950)
- Huber and Van Vleck I (1966)
- Huber and Van Vleck II (1972)
- J.H. Van Vleck (Rev Mod Phys; 1978)

MIT

Weisskopf

- M.W.P. Strandberg

Formalism for the Calculation of Spectral Absorption Coefficients II

$$k(\nu) = \nu \left\{ \frac{1 - e^{-hc\nu/kT}}{1 + e^{-hc\nu/kT}} \right\} \qquad \mathrm{Im} < f(\nu) + f(-\nu) >$$

$$k(\nu) = \nu \;\tanh(hc\nu/2kT) \qquad \mathrm{Im} < f(\nu) + f(-\nu) >$$

radiation field — molecular system ⇔ radiation interaction

(line shape)

<symmetrized spectral density function>

- Radiation balance is satisfied over the full extent of the spectral line irrespective of accuracy of $f(\nu)$!
- F-sum rule rigorously satisfied: integral over ν □ value of the band strength
- Led to the development of the CKD continuum model

Impact Result:

$$k(\nu) \approx \nu \left\{ \frac{1 - e^{-hc\nu/kT}}{1 + e^{-hc\nu/kT}} \right\} < \tilde{S}_i(T) \frac{1}{\pi} \left[\frac{\alpha_i P}{(\nu_i + \nu)^2 + (\alpha_i P)^2} + \frac{\alpha_i P}{(\nu_i - \nu)^2 + (\alpha_i P)^2} \right] >$$

Microwave:

$$\approx \frac{hc\nu^2}{2kT} < \tilde{S}_i(T) \frac{1}{\pi} \left[\frac{\alpha_i P}{(\nu_i + \nu)^2 + (\alpha_i P)^2} + \frac{\alpha_i P}{(\nu_i - \nu)^2 + (\alpha_i P)^2} \right] >$$

Van Vleck - Weisskopf
e.g. Gross, etc. xxx

Infrared:

$$\approx \nu \quad < \tilde{S}_i(T) \frac{1}{\pi} \left[\frac{\alpha_i P}{(\nu_i - \nu)^2 + (\alpha_i P)^2} \right] >$$

Lorentz

Line Shape Issues

Line Shape including widths, shifts and line coupling coefficients is the dominant source of error in current radiance calculations

• Doppler	Gaussian	
• Collisional	Lorentzian	*frequency of collision: (P/T)*
• Voigt	Convolution of Gaussian with Lorentzian	
• Duration of collision	Impact approximation is just that:	*line wings must decay exponentially*
• Speed Dependent Voigt	Doppler and Collisional processes are not independent	
• Line Coupling	Collisional relaxation matrix between lines required	

Water Vapor Spectroscopic Parameters

- **Line Strengths**
  - **Laurent Coudert**
    - » **Strong Lines (mid IR): Intensities increased by ~ 5 %**
    - » **Not an issue for Far Infrared (Pure Rotational region) ???**

- **Line Widths and Shifts / Temperature Dependence**
  - **Bob Gamache & HITRAN**
  - **Present Results**

- **Line Coupling**
  - **Linda Brown (two line resonances)**
  - **Revised relaxation rates**
  - **First Order**
  - **Present Result (400 cm-1)**

- **Continuum**
  - **Inextricably linked to the width**
  - **Scaled in selected regions of the water bands**

Two Closure Studies in the Far Infrared:

1) AERI_ex at ARM NSA Site

A far-infrared radiative closure study in the Arctic: Application to water vapor

J. S. Delamere, S. A. Clough, V. H. Payne, E. J. Mlawer, D. D. Turner, and R. R. Gamache

Radiance Data:

- Linear scaling of radiance in low wavenumber region
- Removal of linearly increasing sinusoid in low wavenumber region
- Average of 5 cases
- Atmosphere: Sondes

2) REFIR-PAD at Cerro Tocco (Chile) & Pagosa Springs (Colorado) RHUBC II

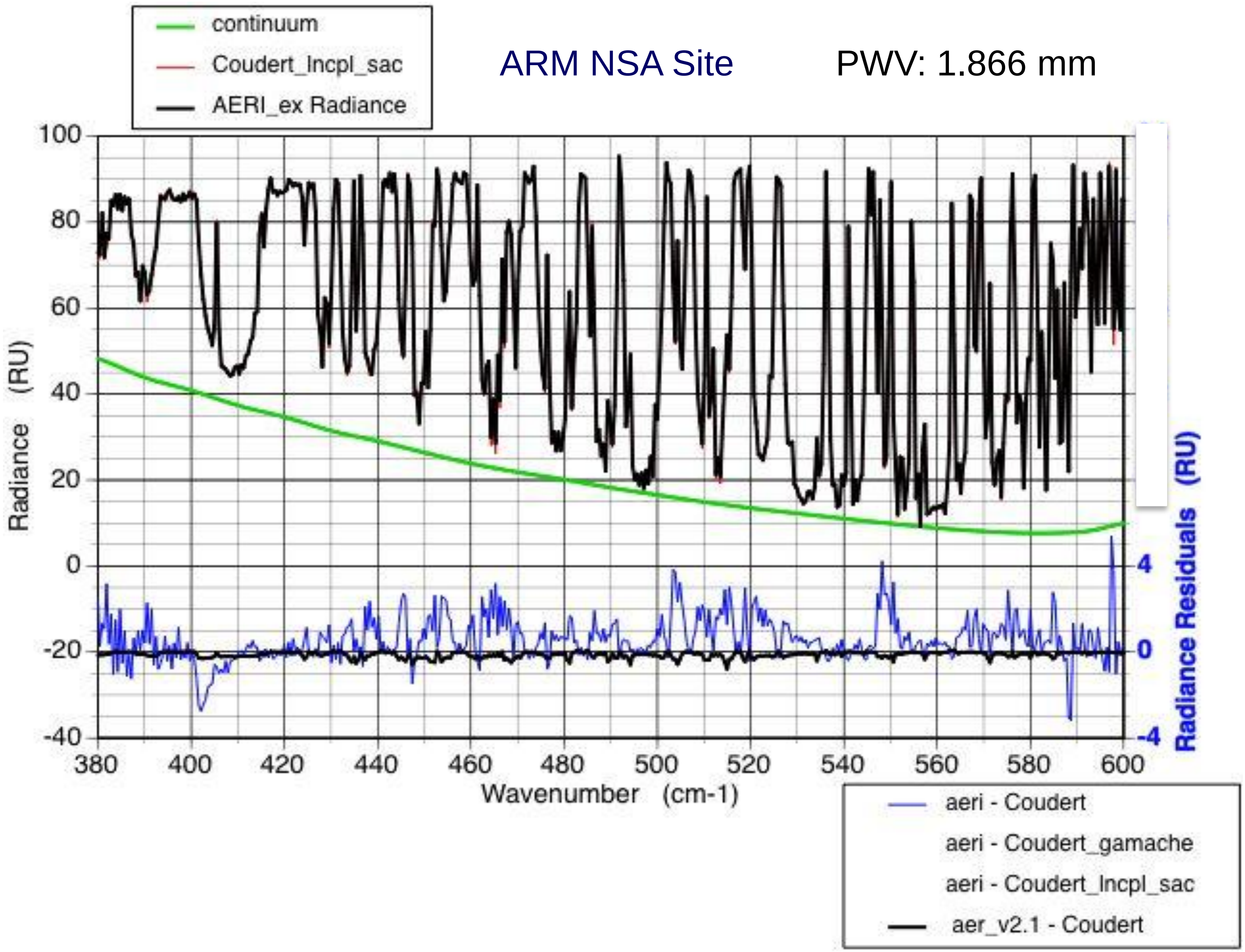
Laboratory characterisation of the Radiation Explorer in the Far-Infrared Breadboard (REFIR/ BB) for the atmospheric emission measurement in the 100-1100 cm^{-1} spectral range

Luca Palchetti(1), Giovanni Bianchini(1), Carmine Serio(2), Francesco Esposito(2), Rolando Rizzi(3), Vincenzo Cuomo(4)

Data:

- Average of five spectra
- Linear scaling of radiance in low wavenumber region
- Atmosphere: Retrieved; *a priori:* sondes

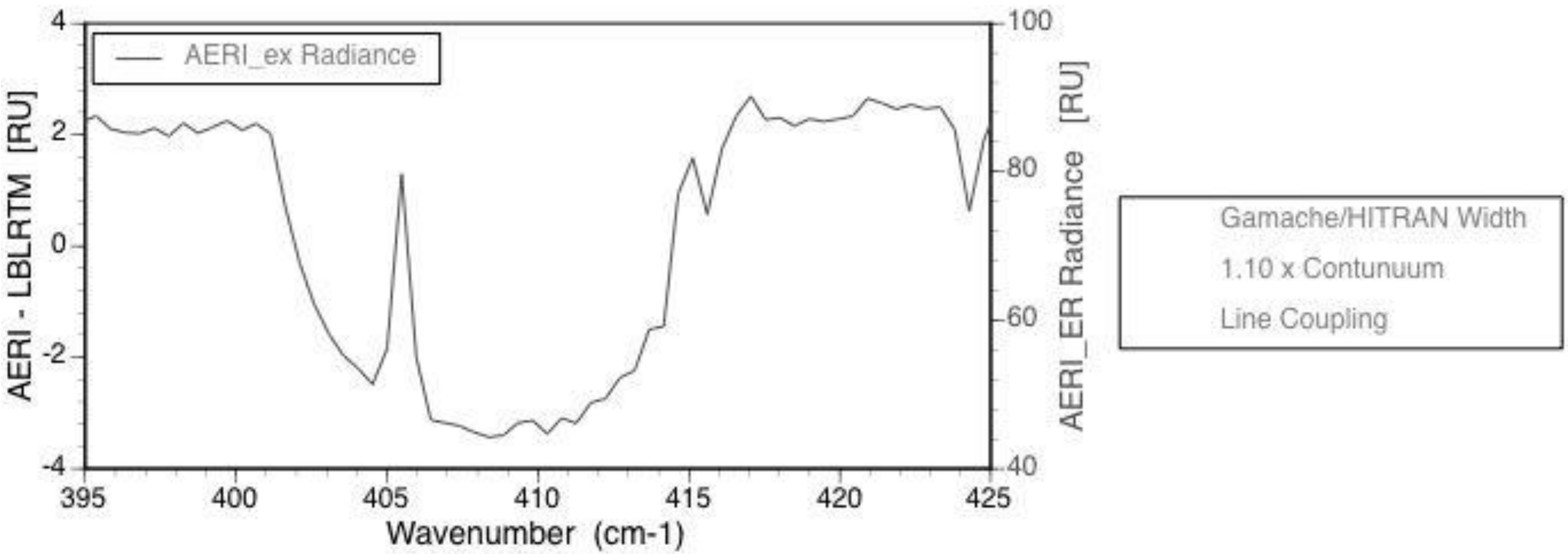
AERI Downwelling Radiances I



AERI Downwelling Radiances II

ARM NSA Site

Line Coupling



Residual at 400cm-1

Line Coupling to Resolve the Residual
This Work

Transition Fequency										Strength	Gamache Width	% change	CRA Width	Self Widths	ln cpl 296K
398.976493		9	7	2		8	6	3		5.556D-20	0.0414	-13.0	0.0360	0.328	
400.221796		10	4	6		9	3	7		1.070D-20	0.0791	0.0	0.0791	0.301	0.013000
400.481057		10	6	4		9	5	5		1.071D-20	0.0510	0.0	0.0510	0.301	-0.013038

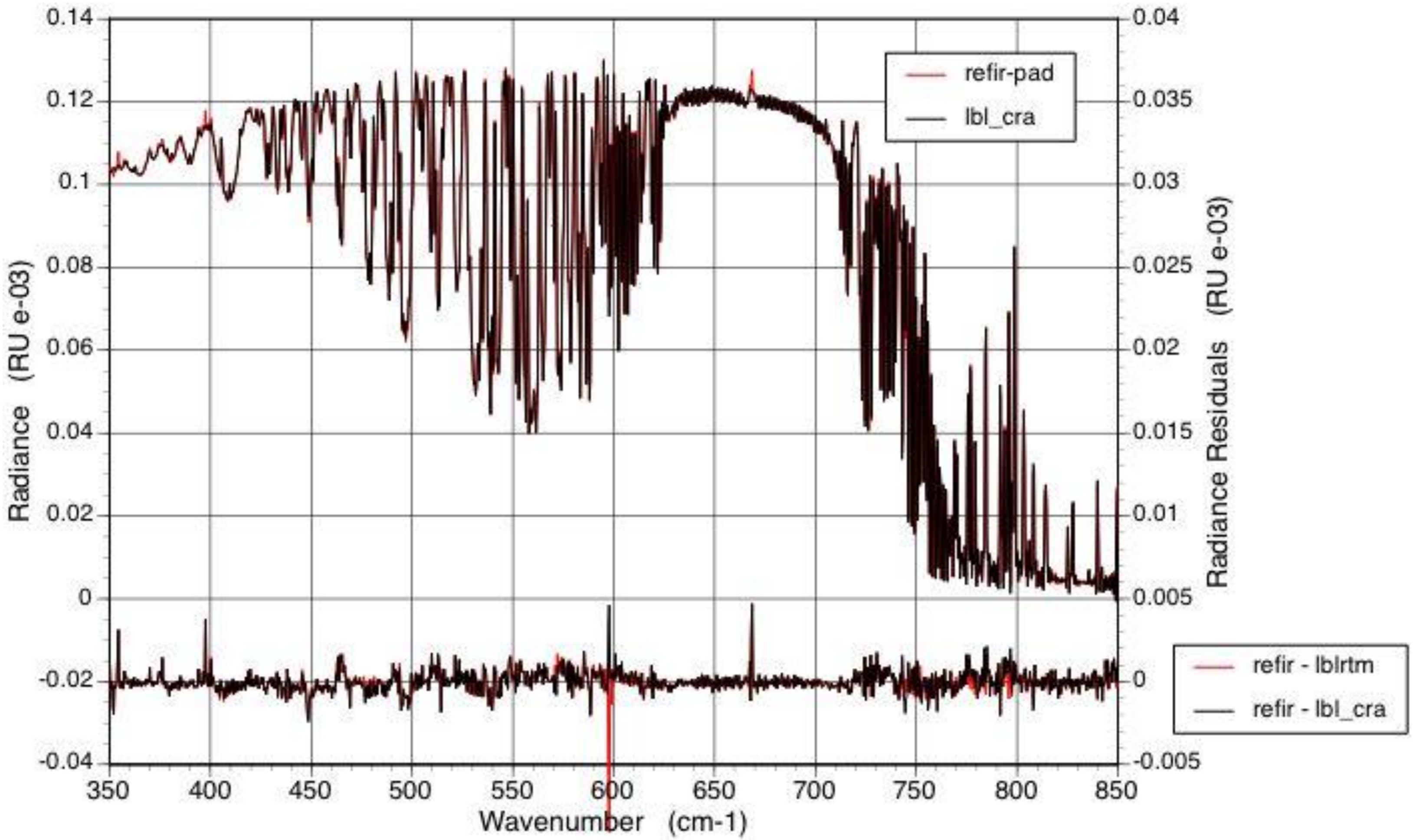
Half Width Adjustments to Resolve the Residual
Delamere et al.

Transition Frequency										Strength	Gamache Width	% Change	"Clough Width"	Self Width
396.432560		8	2	6		7	1	7		2.396E-20	0.0807	-7.5	0.0746	0.384
397.318923		9	3	6		8	2	7		5.811E-20	0.0804	-7.5	0.0743	0.328
397.675624		10	6	5		9	5	4		3.104E-20	0.0565	-7.5	0.0522	0.301
398.941390		9	7	3		8	6	2		1.825E-20	0.0415	-20.5	0.0330	0.328
398.976486		9	7	2		8	6	3		5.476E-20	0.0414	-20.5	0.0329	0.328
400.221819		10	4	6		9	3	7		1.053E-20	0.0791	-25.0	0.0593	0.301
400.481040		10	6	4		9	5	5		1.051E-20	0.0510	-25.0	0.0383	0.301

REFIR_PAD 20090425 Pagosa Springs, CO RHUBC II

Retrieved atmosphere a piori: sonde

L	PATH (km)	PBAR	TBAR	P_h2o (mb)	T_h2o(K)	PWV (cm)	O3 (du)
22	2.33-18.00	414.86	251.72	606.20	268.86	**0.6441**	124.27



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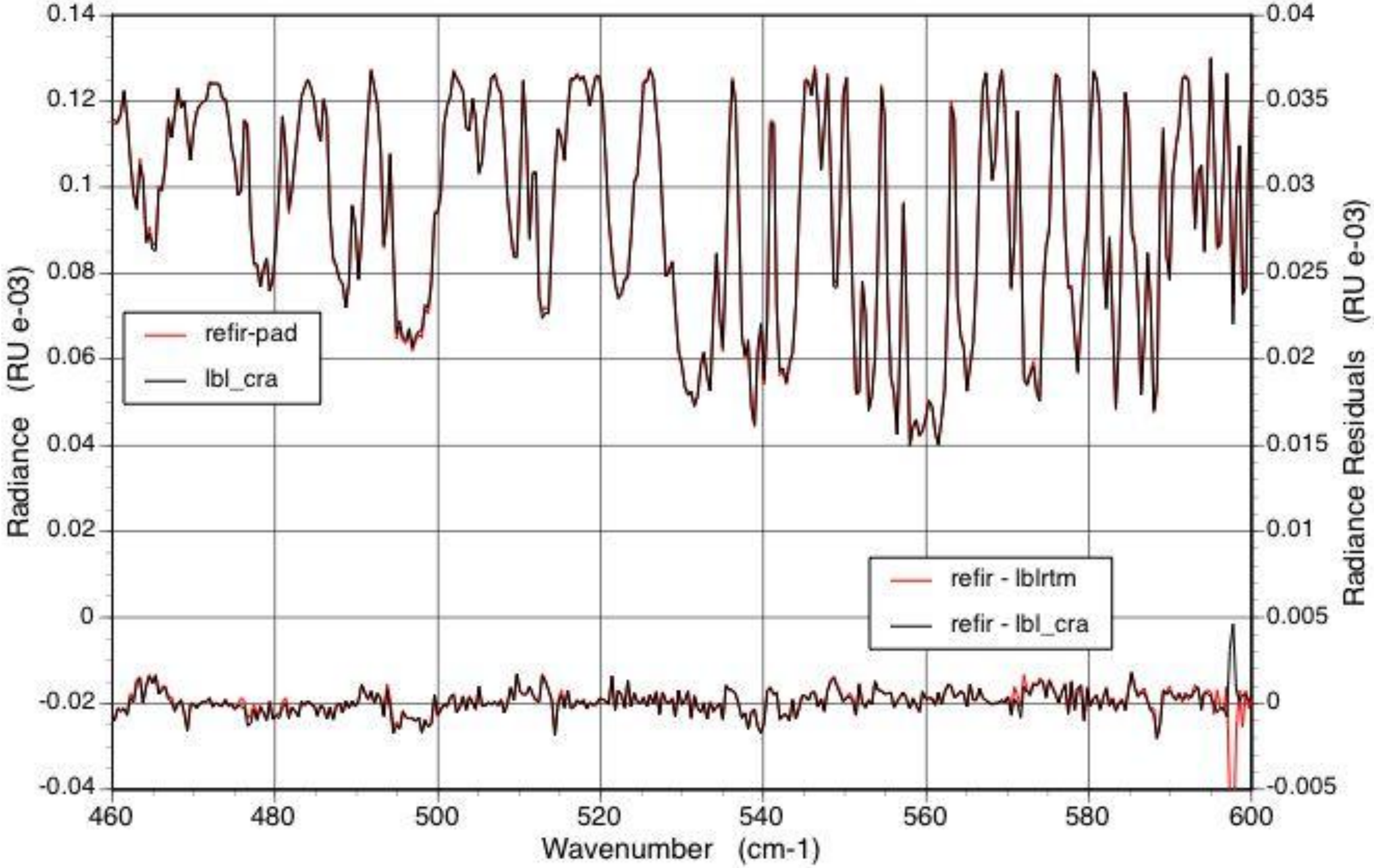
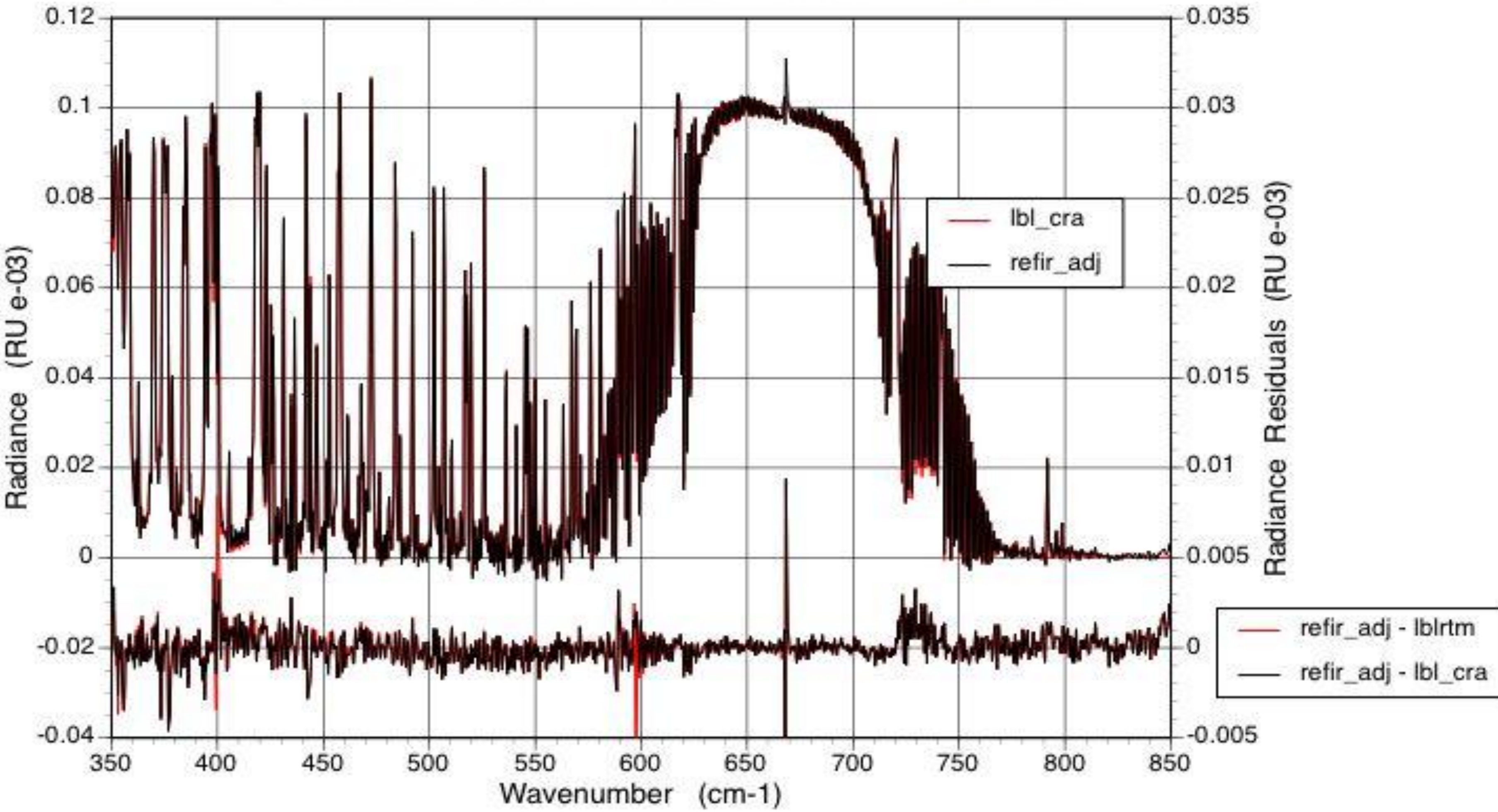


REFIR_PAD 20090919 CERRO TOCO (5383M) RHUBC II

Retrieved atmosphere a piori: sonde

L	PATH (km)	PBAR	TBAR	P_h2o (mb)	T_h2o(K)	PWV (cm)	O3 (du)
19	5.383-18.000	305.70	234.85	388.01	249.24	**0.0247**	28.1



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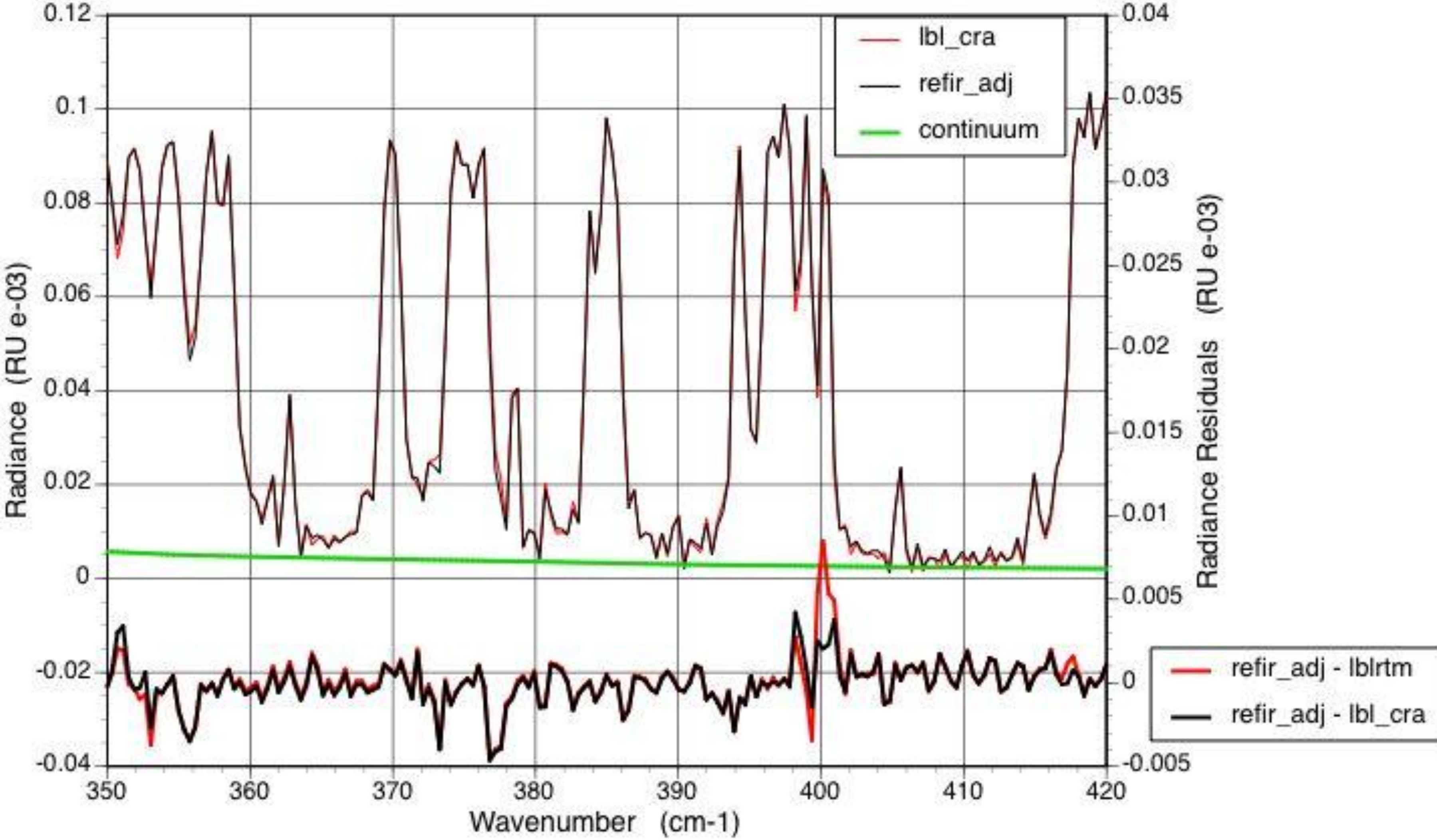

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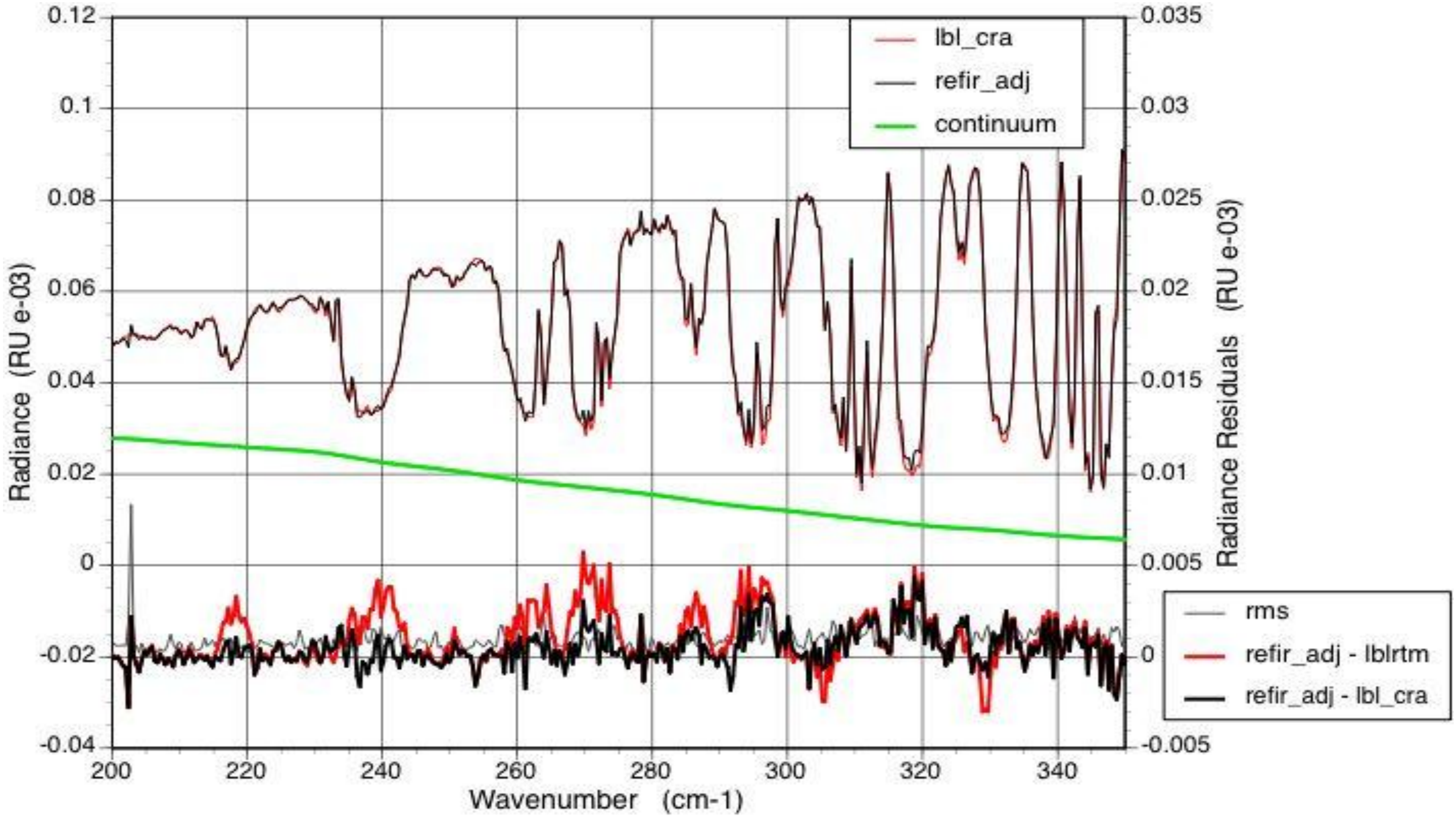
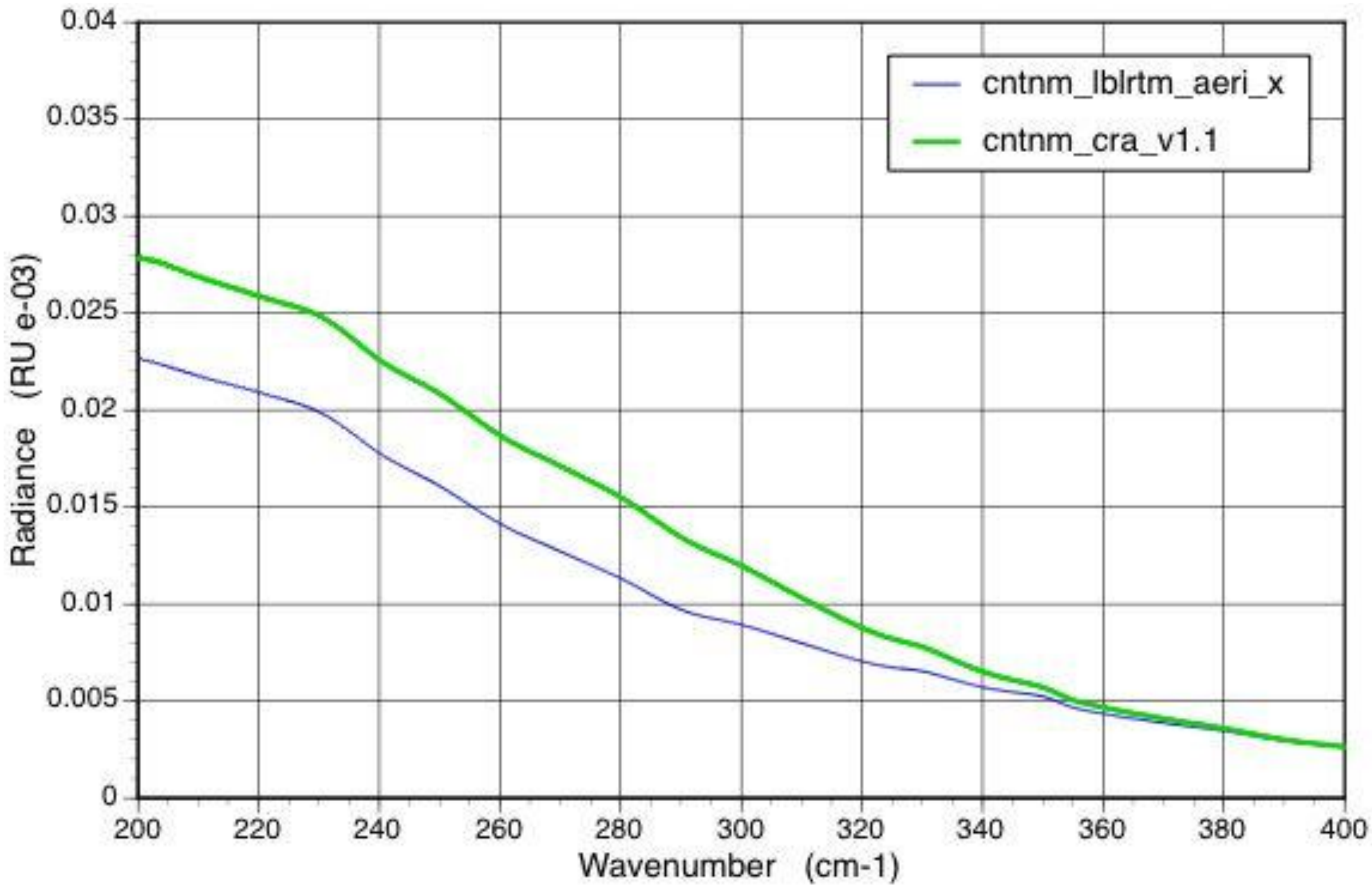


Continuum

REFIR_PAD 20090919 CERRO TOCO (5383M) RHUBC II



Continuum

CKD Continuum (1980)

- Direct consequence Van Vleck's paper
- Line at 100 cm-1 is greatest contributor to continuum at 1000 cm-1
- Detail balance satisfied
- Exponential decay of far wings
- Works remarkably well
- Line shape *engineering*
  - 6 parameters
- Inter-molecular Potential *engineering*
  - Ma and Tipping
- Super Lorentzian line shape to obtain observed 'extra absorption'

MT_CKD Continuum

- Super Lorentzian line shape is untenable
- Collision Induced Model introduced to attain 'extra absorption
- Direct consequence of the our work on Oxygen at 7900 cm-1

Oxygen Continuum

MLAWER ET AL.: ATMOSPHERIC COLLISION-INDUCED ABSORPTION

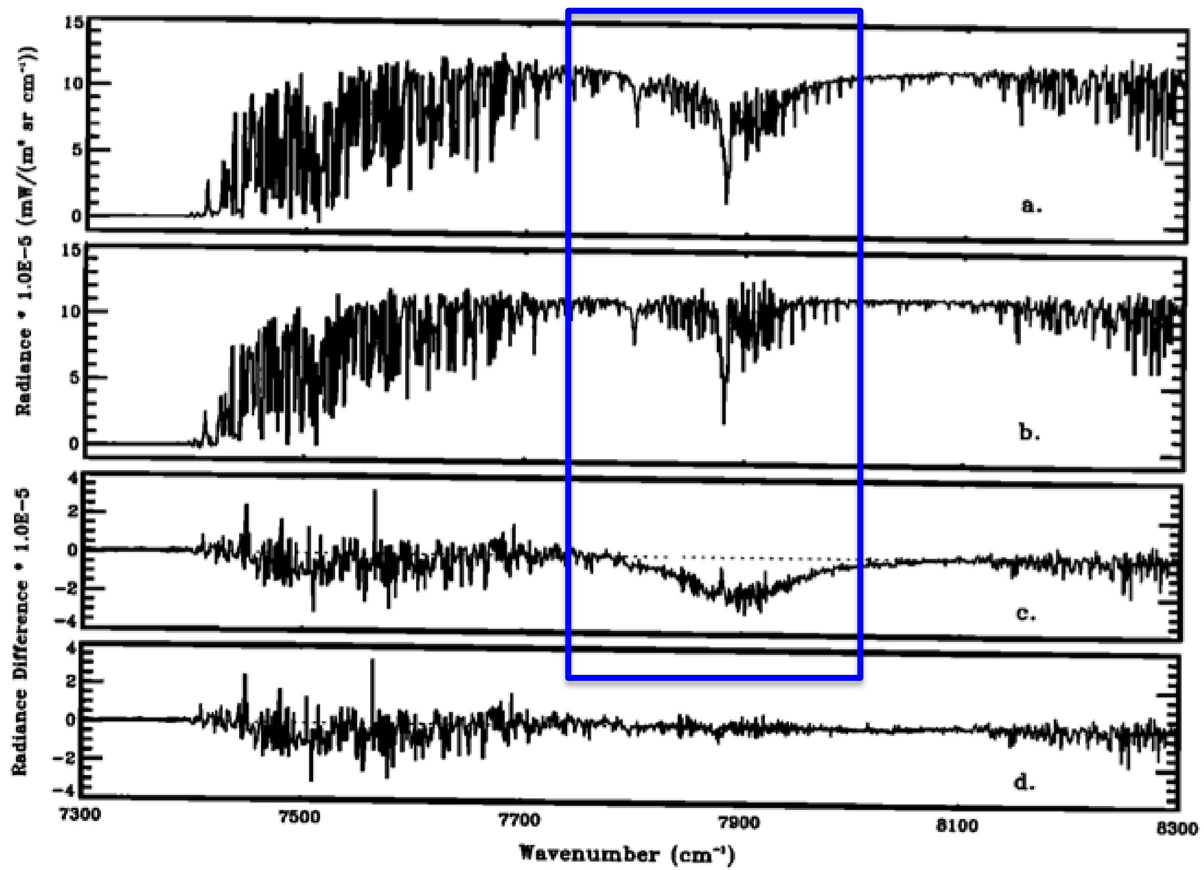
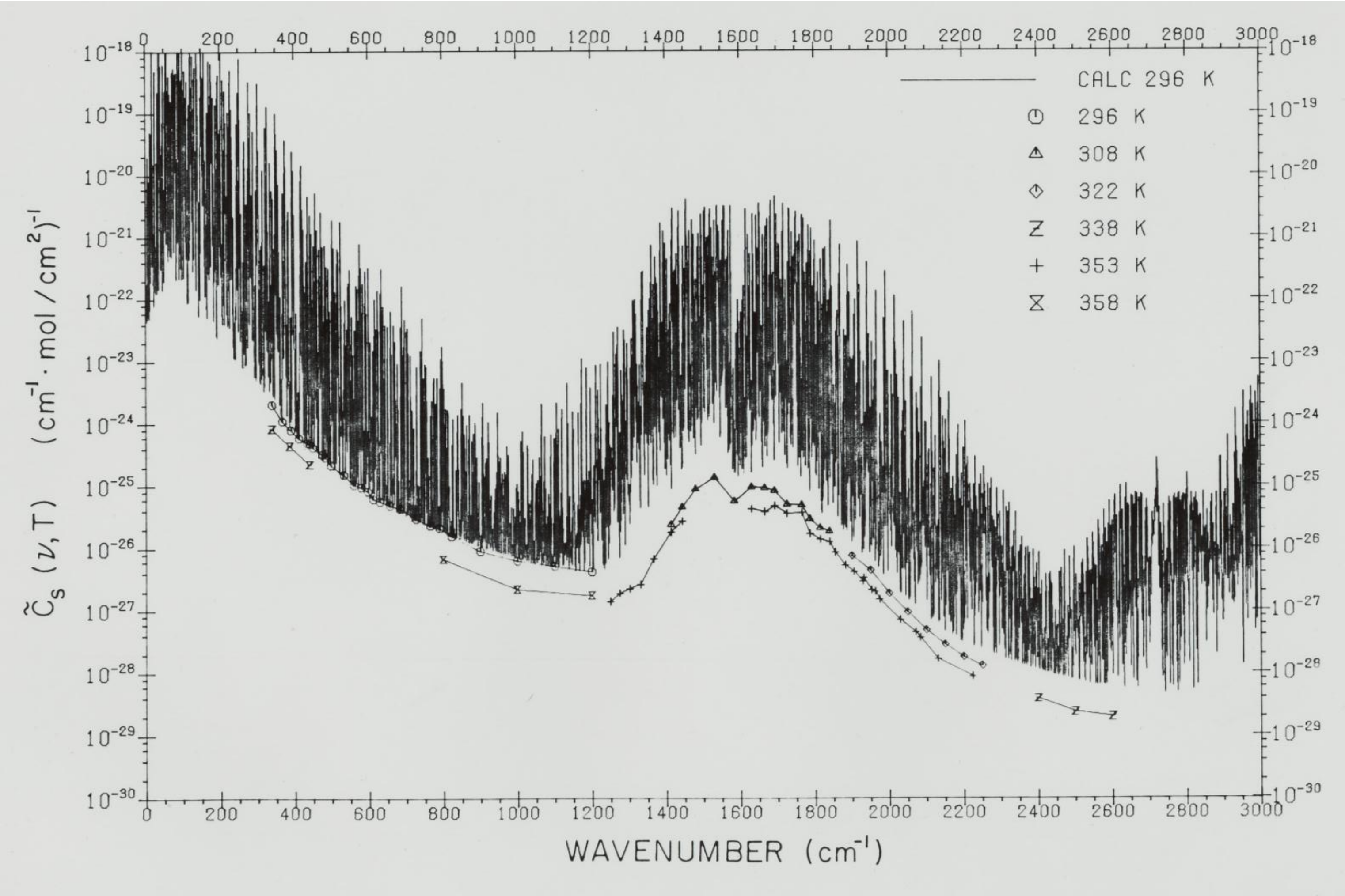
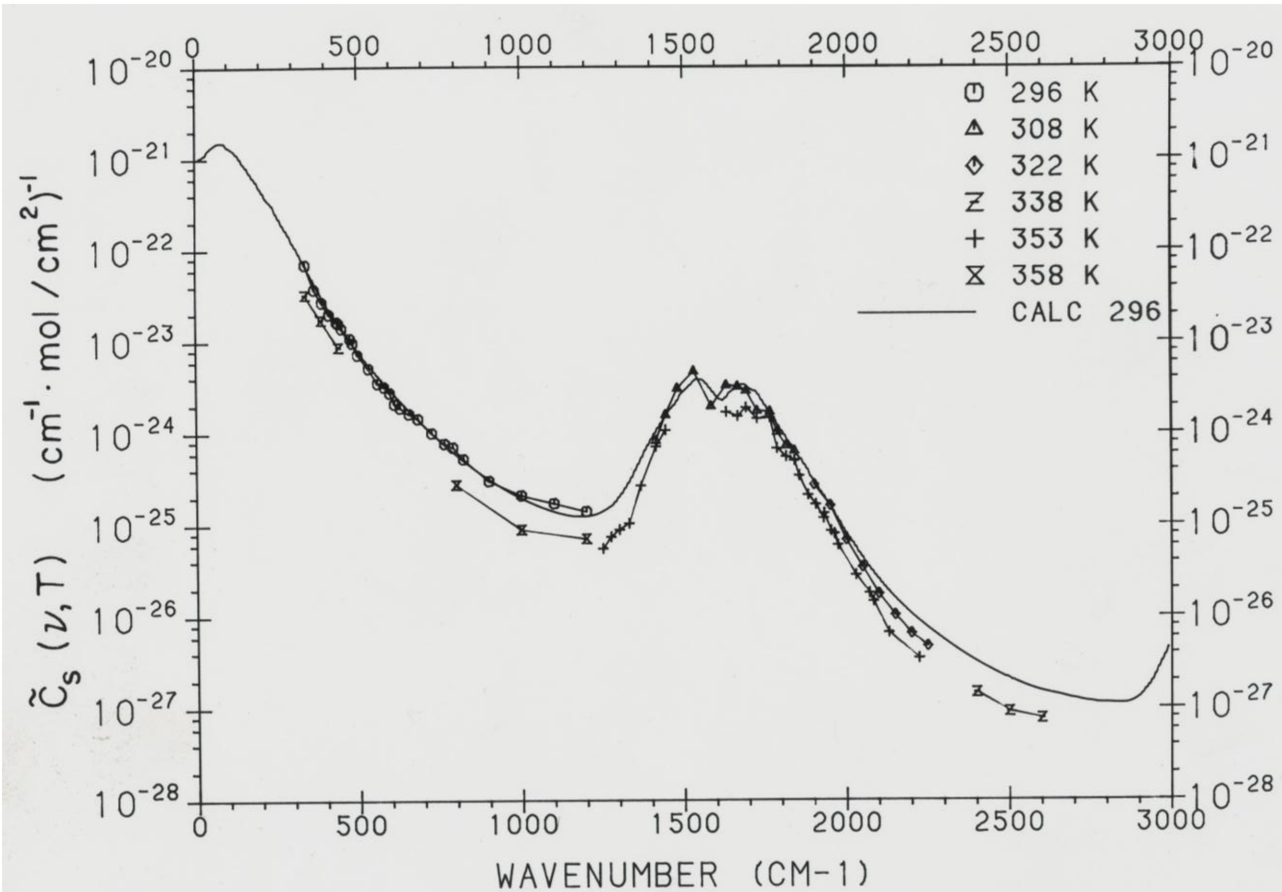


Figure 1. (a) Solar radiances measured with the Absolute Solar Transmittance Interferometer (ASTI), (b) radiances calculated by the line-by-line radiative transfer model (LBLRTM), (c) differences between the ASTI measured radiances and the LBLRTM calculated radiances before formulation of the O_2 continuum, and (d) differences between the ASTI measured radiances and the LBLRTM calculated radiances after formulation of the O_2 continuum for the spectral range 7300–8300 cm^{-1} and a zenith angle of 71.5°.

CKD Continuum

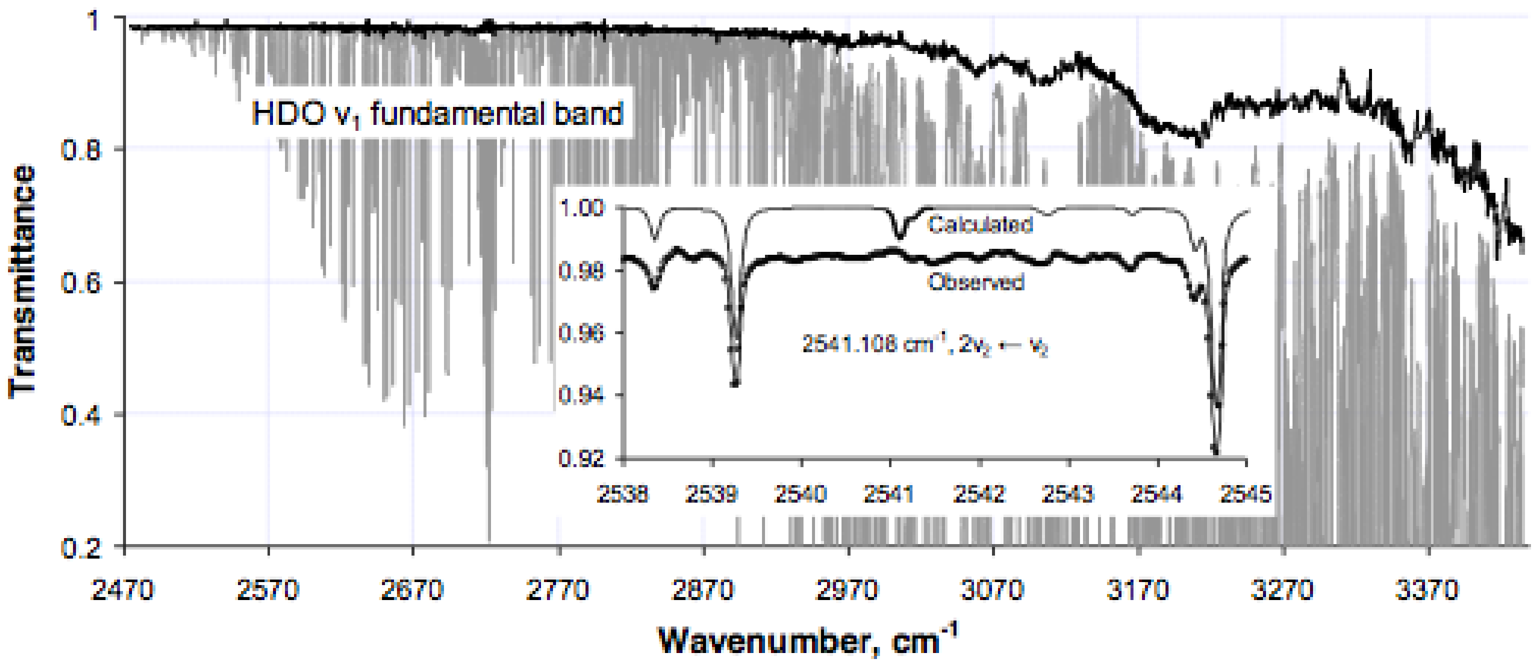


Continuum



296 K
308 K
322 K
338 K
353 K
358 K
CALC 296
$\tilde{C}_s$ (ν,T) (cm^{-1} · mol / cm^2)$^{-1}$
WAVENUMBER (CM-1)
0
500
1000
1500
2000
2500
3000
10^{-20}
10^{-21}
10^{-22}
10^{-23}
10^{-24}
10^{-25}
10^{-26}
10^{-27}
10^{-28}

Baranov and Lafferty



the window around 2500 cm^{-1} (see inset) the continuum plots look quite smooth. Note, however, that there is a distinct feature around 3200 cm^{-1}. Recently this has been observed also by Paynter *et al*. [17, 18]. Their continuum data at 351 K in the range between 3025 cm^{-1} and 3400 cm^{-1} are in good agreement with ours. The intensity of the feature at 3200 cm^{-1} appears to decrease as the temperature grows and, presumably, it belongs to the overtone of the O-H-O bending mode of the water dimer at 3215 cm^{-1}, which has been predicted in theoretical calculations by Schofield and Kjaergaard [23]. Much weaker structures in the regions 1925 cm^{-1} to 2025 cm^{-1} and 3300 cm^{-1} to 3500 cm^{-1} are still not understood as are similar weak structures in the 10 μm region [11].

"Extra Absorption" Incorporated in the Continuum

Collision Induced Model (MT_CKD)

Binary Collisions
Monomer Transitions
Agreement with Reliable DATA with minimal parameters is compelling
Line Widths result from Duration of Collision Time
Genesis from the CIA in the Oxygen Band at 7900 cm-1
Collision Induced Absorption in CO has recently been observed

Dimer (Bound) Model

Not consistent with Binary Collisions
How is the population sustained?
No compelling spectral evidence (that I've seen)
Not that there couldn't be if done properly

CAVIAR

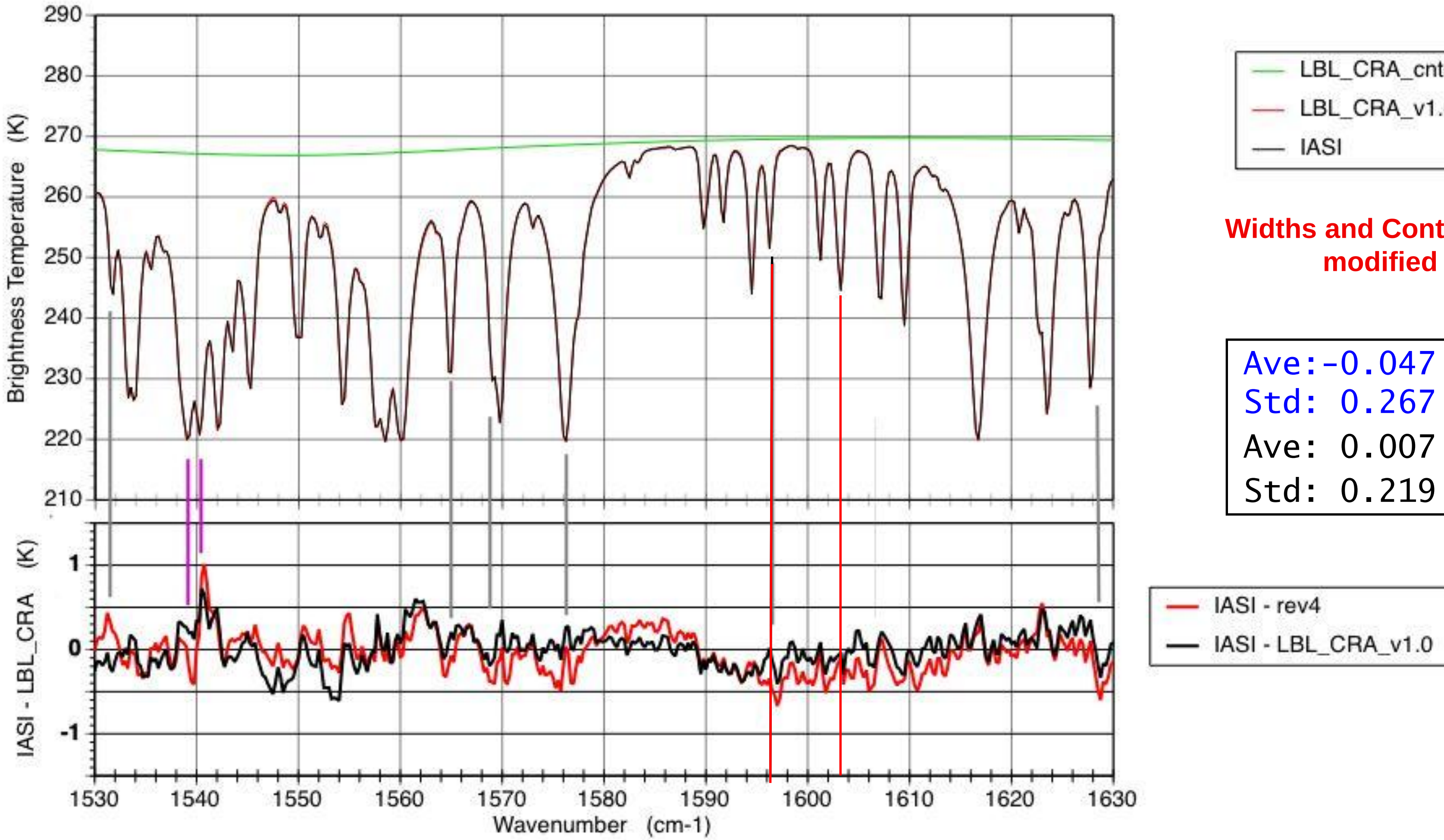
Avenging the mistakes of King George III ??? (facetious of course)
Analyses have simply been inadequate
Recent articulation: the spectra are due to monomer transitions in a loosely bound dimer

Summary

- Energetically the Far Infrared is Crucial
- Formalism for Calculations of Radiance from the Microwave to UV is well Established
- The Measurements from AERI_ex and REFIR_PAD are just beautiful
- Bravo to NSA and RHUBC II Campaigns
- Major Spectroscopic Issue: Line Widths
- Line Strengths: Strong Lines generally good; Weak Lines in need of improvement
- Spectroscopy in Absorption Windows is Extremely Important
  - Continuum Value Interlinked with Widths
  - Not presently being done properly!!!
  - Higher Resolution is Critical for future improvement
- In my view, Collision Induced Absorption is the most Reasonable Explanation of Extra Absorption
- CAVIAR Initiative is Highly Disappointing (Distressing)

  King George III Effect

Water Vapor Band Center: 1530 -1630 cm-1



Widths and Continuum modified

Ave:-0.047 K
Std: 0.267 K
Ave: 0.007 K
Std: 0.219 K

Line Coupling 1540 cm-1

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Line Coupling: Accidental Line Resonances

400 cm-1 Tony Clough

```
11  398.976493 5.556D-20 2.283E+01.0360.3283 1411.61150.29-.000910  1  1 9 7 2    8 6 3   5552433 5
11  400.221796 1.070D-20 4.643E+00.0791.3009 1216.23130.710.004940  1  110 4 6    9 3 7   5552433-1
1 1.456529E-01           1.365260E-01           1.300000E-01           1.248789E-01            -1
11  400.481057 1.071D-20 1.636E+01.0510.3009 1474.98080.30-.000770  1  110 6 4    9 5 5   5552433-1
1-2.671053E-01          -1.725650E-01          -1.303796E-01          -1.064366E-01            -1
```

Y: 200K 250K 296K 340K

1540 cm-1 Linda Brown

```
11 1539.060760 2.255D-19 1.153E+01.1053.4643   79.49640.79-.004100  2  1 1 0 1    2 1 2   3555433-1
1 1.098843E-02           1.048538E-02           1.012000E-02           9.829722E-03            -1

11 1540.299806 1.767D-19 7.175E+00.0971.5173  136.76170.79-.000020  2  1 2 1 2    3 0 3   3577443-1
1-1.604015E-02          -1.409560E-02          -1.292537E-02          -1.211058E-02            -1
```

1630 cm-1 Linda Brown


```
11 1539.060760 2.255D-19 1.153E+01.1053.4643   79.49640.79-.004100  2  1 1 0 1    2 1 2   3555433-1
1 1.098843E-02           1.048538E-02           1.012000E-02           9.829722E-03            -1
11 1540.299806 1.767D-19 7.175E+00.0971.5173  136.76170.79-.000020  2  1 2 1 2    3 0 3   3577443-1
1-1.604015E-02          -1.409560E-02          -1.292537E-02          -1.211058E-02            -1
```

MT_CKD Water Vapor Continuum Model

- **Definition: Continuum is that absorption with slow spectral dependence which,**

  when added to the line by line absorption, provides agreement with measurement.
- **Scaling: Dependence on pressure, temperature and mixing ratio must be correct**
- **The model is based on contributions from two sources:**

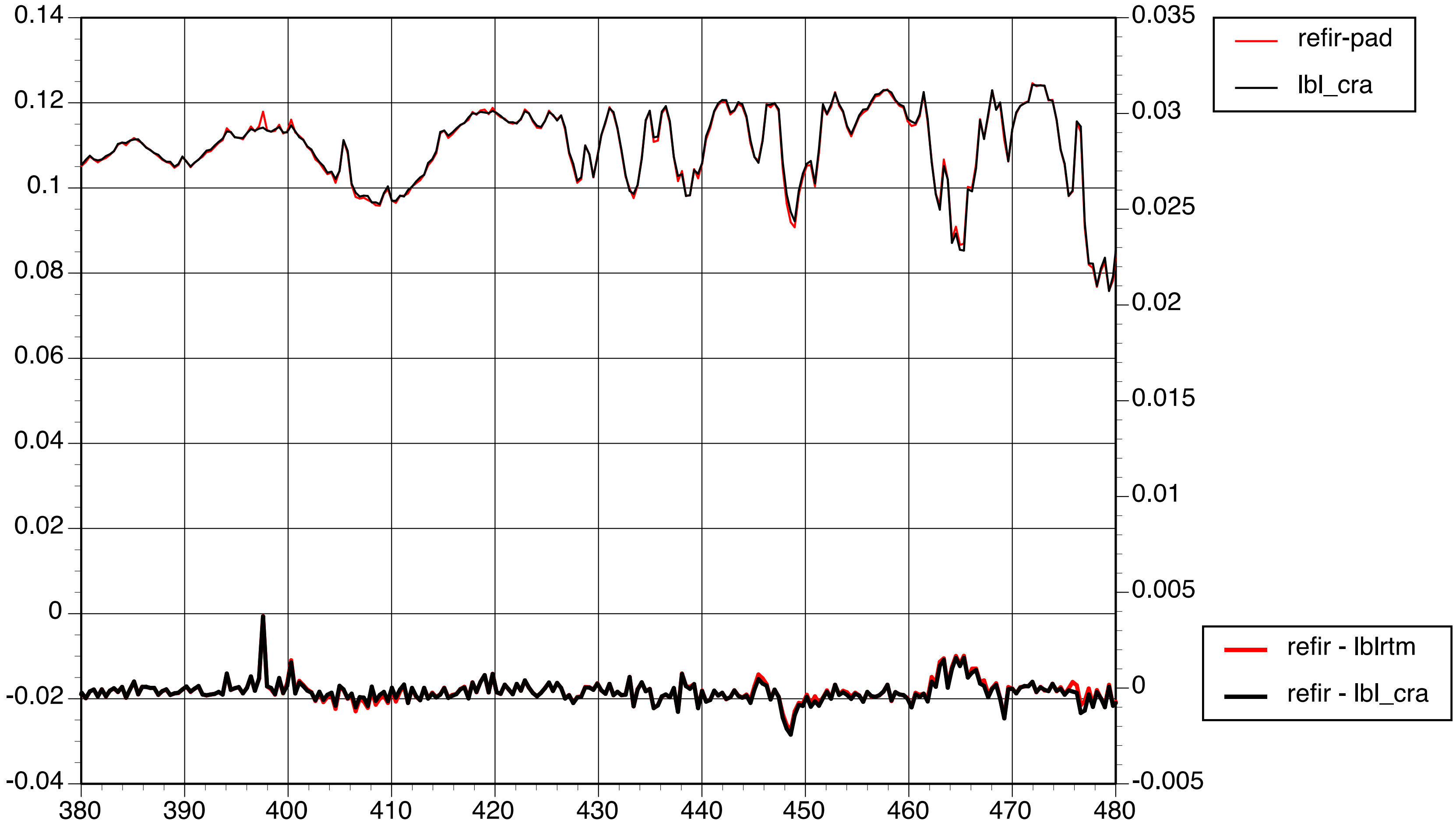
  1. **Allowed line contribution**
     - **Line wing formalism constrained by the known physics with relevant**

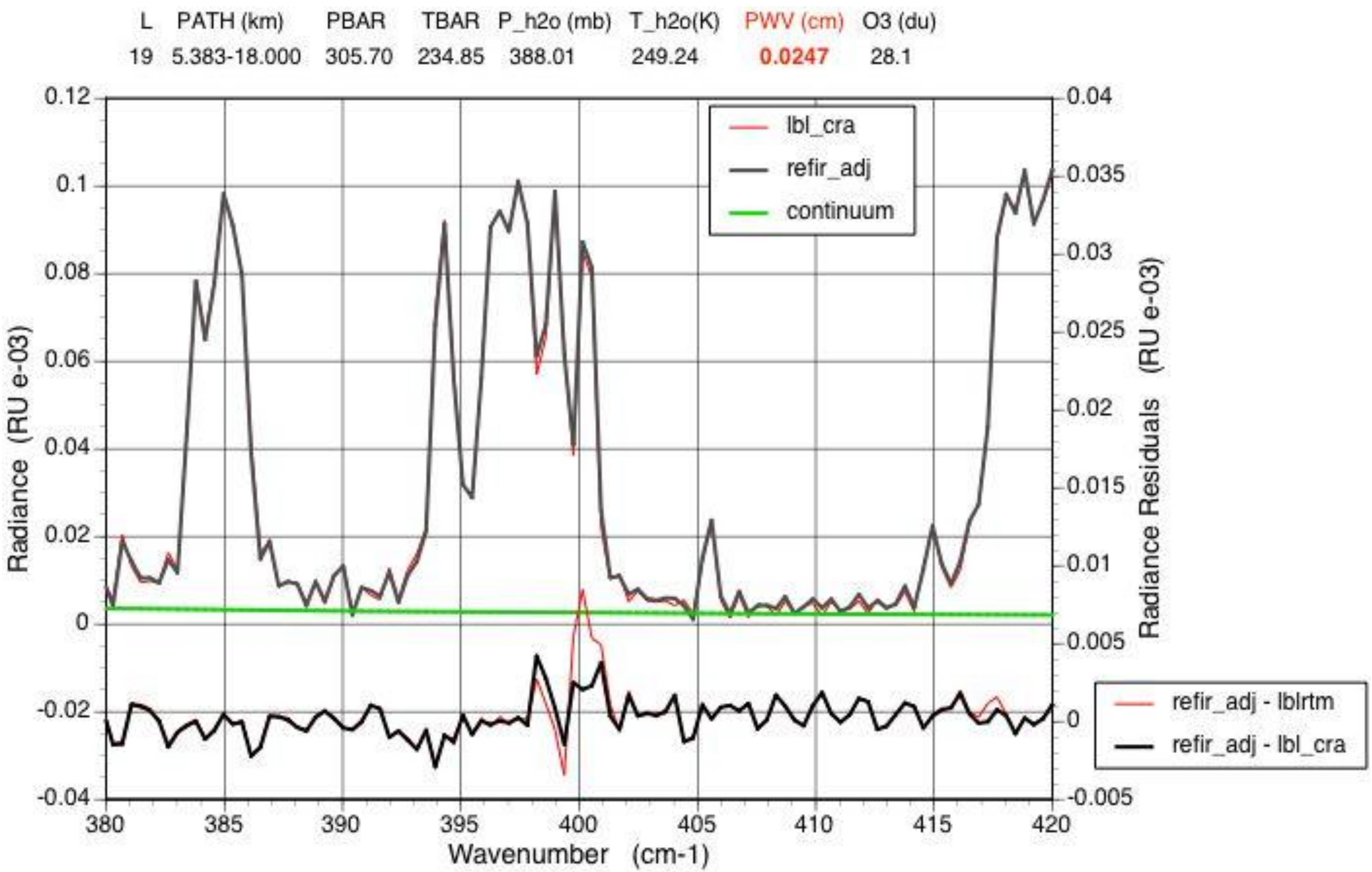
       parameters (~2) determined from laboratory and atmospheric Measurements
     - **Same line shape is used for every line from the Microwave to 20,000 cm-1**
  2. **Collision-Induced contribution**
     - **Provides the extra absorption previously provided by the 'super Lorentzian' chi factor**
     - **Based on dipole allowed transitions with widths ~ 50 cm-1**
     - **Same line shape is used for every line from the Microwave to UV**
- **The model includes both self and foreign continuum**
- **Spectral region: 0 - 20,000 cm^{-1}**

rpad_20090425_1423

RHUBC-II
Pagosa Springs, CO
(after retrieval)

L	PATH (km)	PBAR	TBAR	P_h2o (mb)	T_h2o(K)	PWV (cm)	O3 (du)
22	2.33-18.00	414.86	251.72	606.20	268.86	**0.6441**	124.27

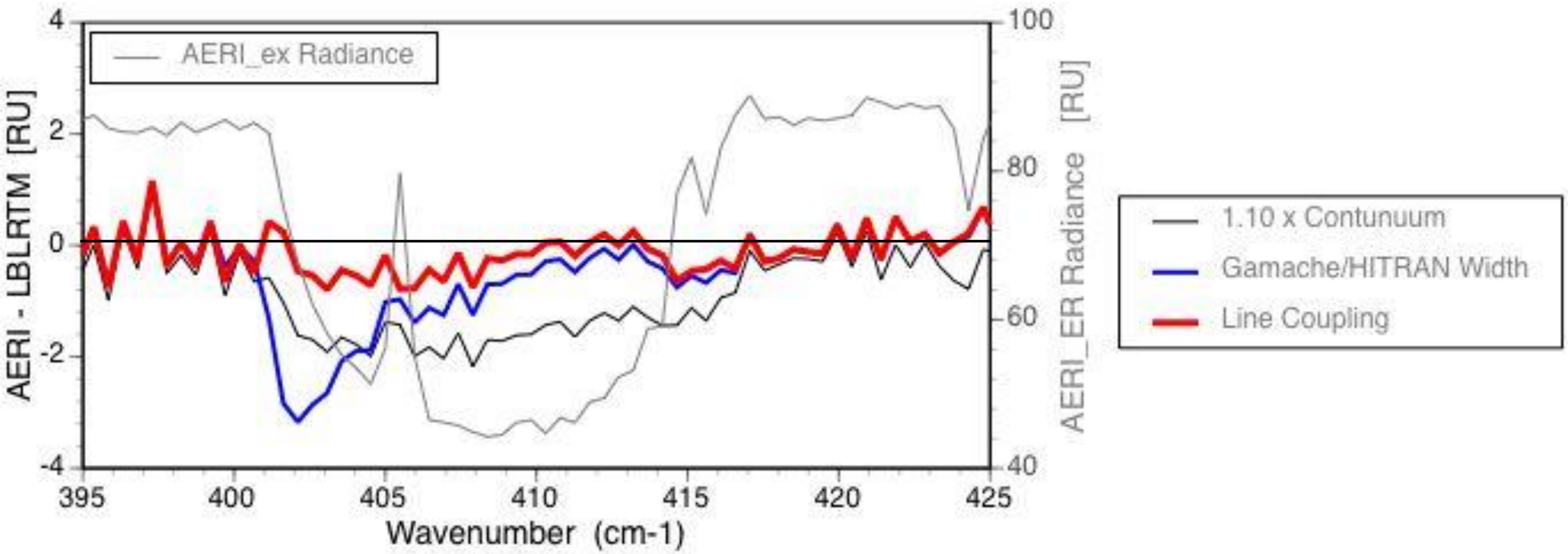



L PATH (km) PBAR TBAR P_h2o (mb) T_h2o(K) PWV (cm) O3 (du)
19 5.383-18.000 305.70 234.85 388.01 249.24 0.0247 28.1
lbl_cra
refir_adj
continuum
refir_adj - lblrtm
refir_adj - lbl_cra
Radiance (RU e-03)
Radiance Residuals (RU e-03)
Wavenumber (cm-1)
0.12
0.1
0.08
0.06
0.04
0.02
0
-0.02
-0.04
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
-0.005
380
385
390
395
400
405
410
415
420

AERI Downwelling Radiances II

ARM NSA Site

Line Coupling



Far- Infrared Workshop, 8 Nov 2011

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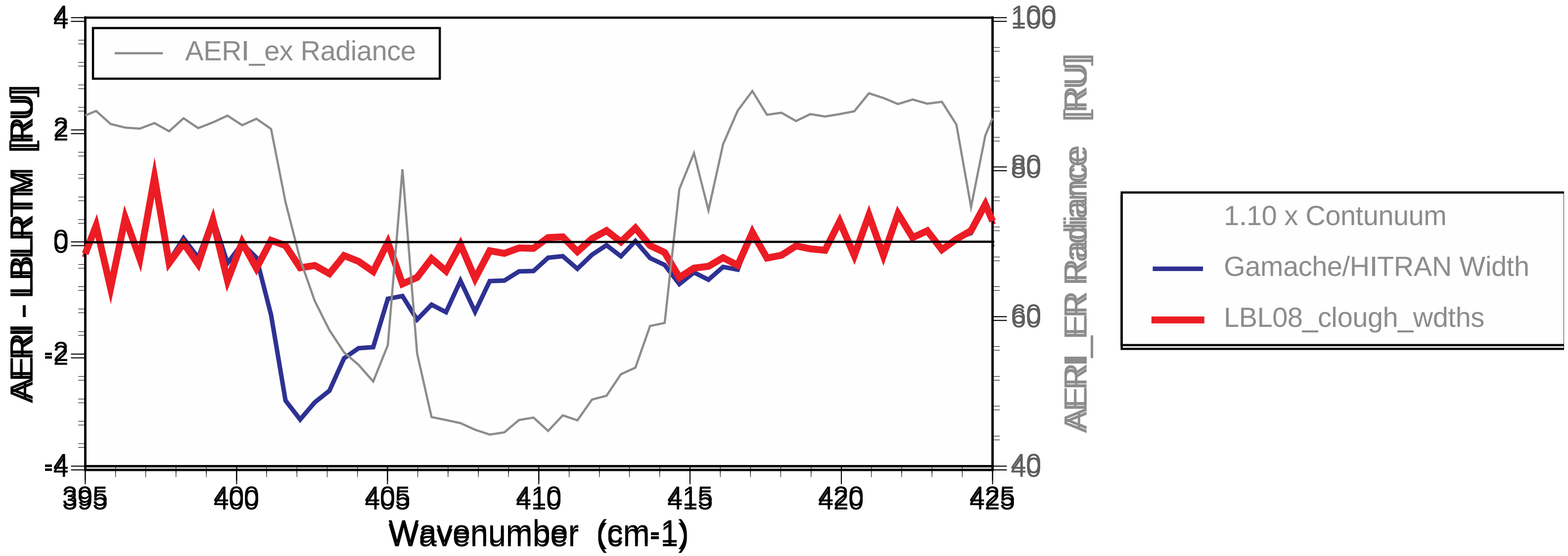
AERI Downwelling Radiances
ARM NSA Site



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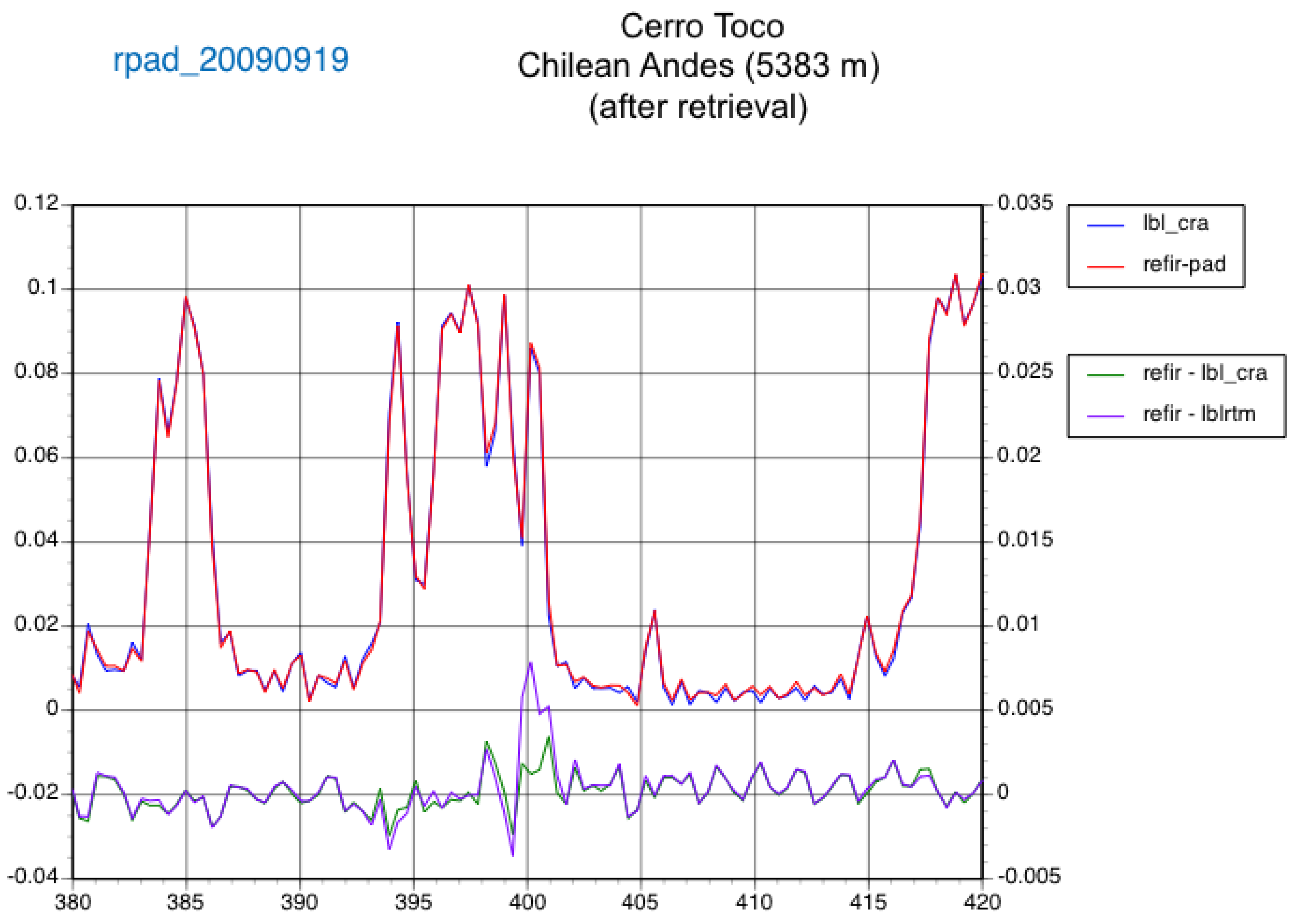
400.481040	10	6	4	9	5	5	1.051E-20	0.0510	-25.0	0.0383	0.301

not JCSDA


rpad_20090919
Cerro Toco
Chilean Andes (5383 m)
(after retrieval)
0.12
0.1
0.08
0.06
0.04
0.02
0
-0.02
-0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
-0.005
380
385
390
395
400
405
410
415
420
lbl_cra
refir-pad
refir - lbl_cra
refir - lblrtm

Impact Approximation »» Duration of Collision »» $\chi(\nu_i - \nu)$ factor

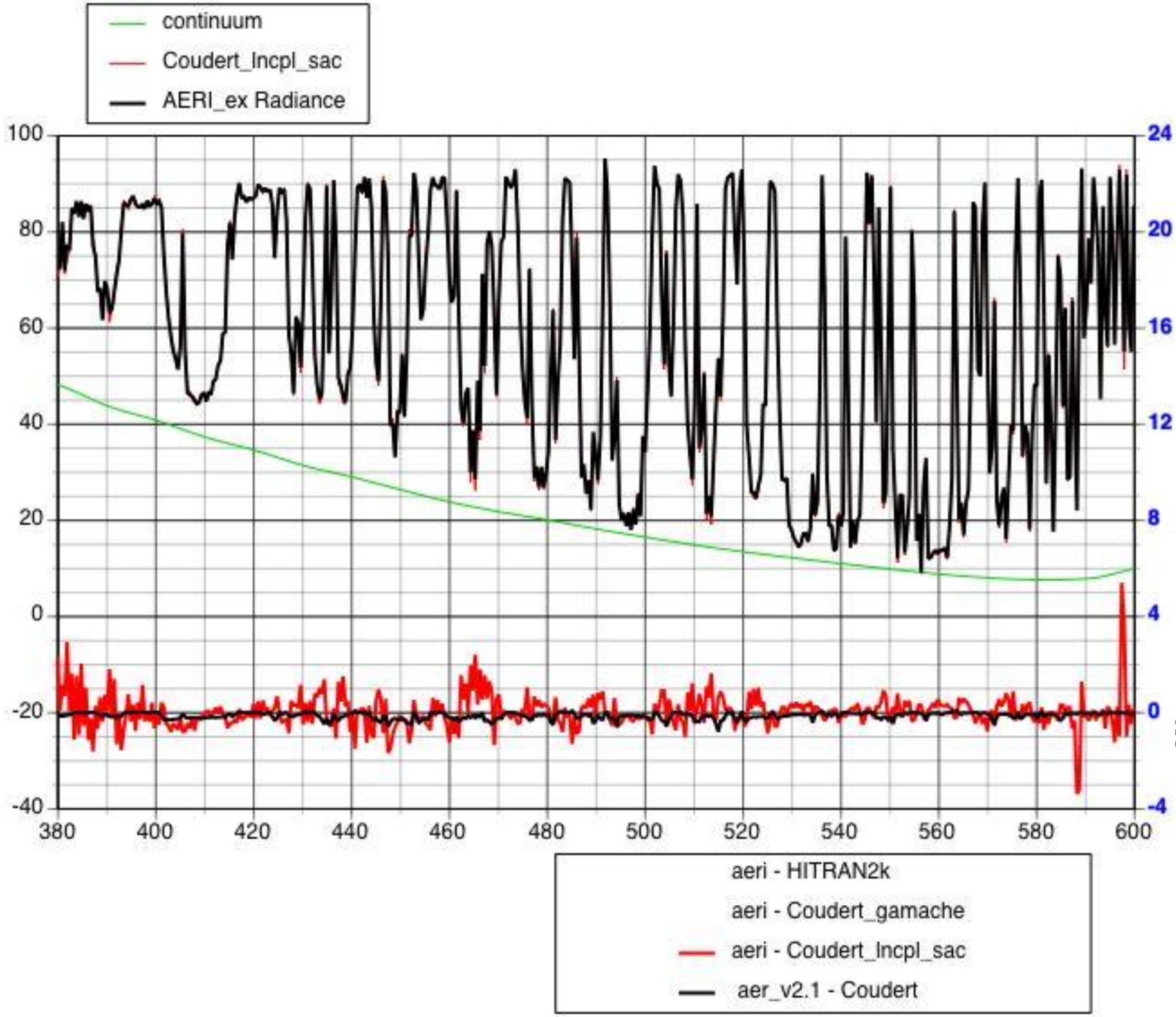
$$k(\nu) \approx \nu \left\{ \frac{1 - e^{-hc\nu/kT}}{1 + e^{-hc\nu/kT}} \right\} < \tilde{S}_i(T)\, \frac{1}{\pi} \left[\frac{\alpha_i P}{(\nu_i + \nu)^2 + (\alpha_i P)^2}\, \chi(\nu_i + \nu) + \frac{\alpha_i P}{(\nu_i - \nu)^2 + (\alpha_i P)^2}\, \chi(\nu_i - \nu) \right] >$$

		grade		grade
$\tilde{S}_i(T)$	Strength	A+		
$\nu_i \Rightarrow \nu_i + \delta_i(P, T)$	Line Position	A++	Pressure Shift	C/D
$\alpha_i \Rightarrow \alpha_i \gamma_i^{T/T_0}$	Width	B	T Dependence	C
$\chi(\nu_i - \nu)$	χ Fn	?		

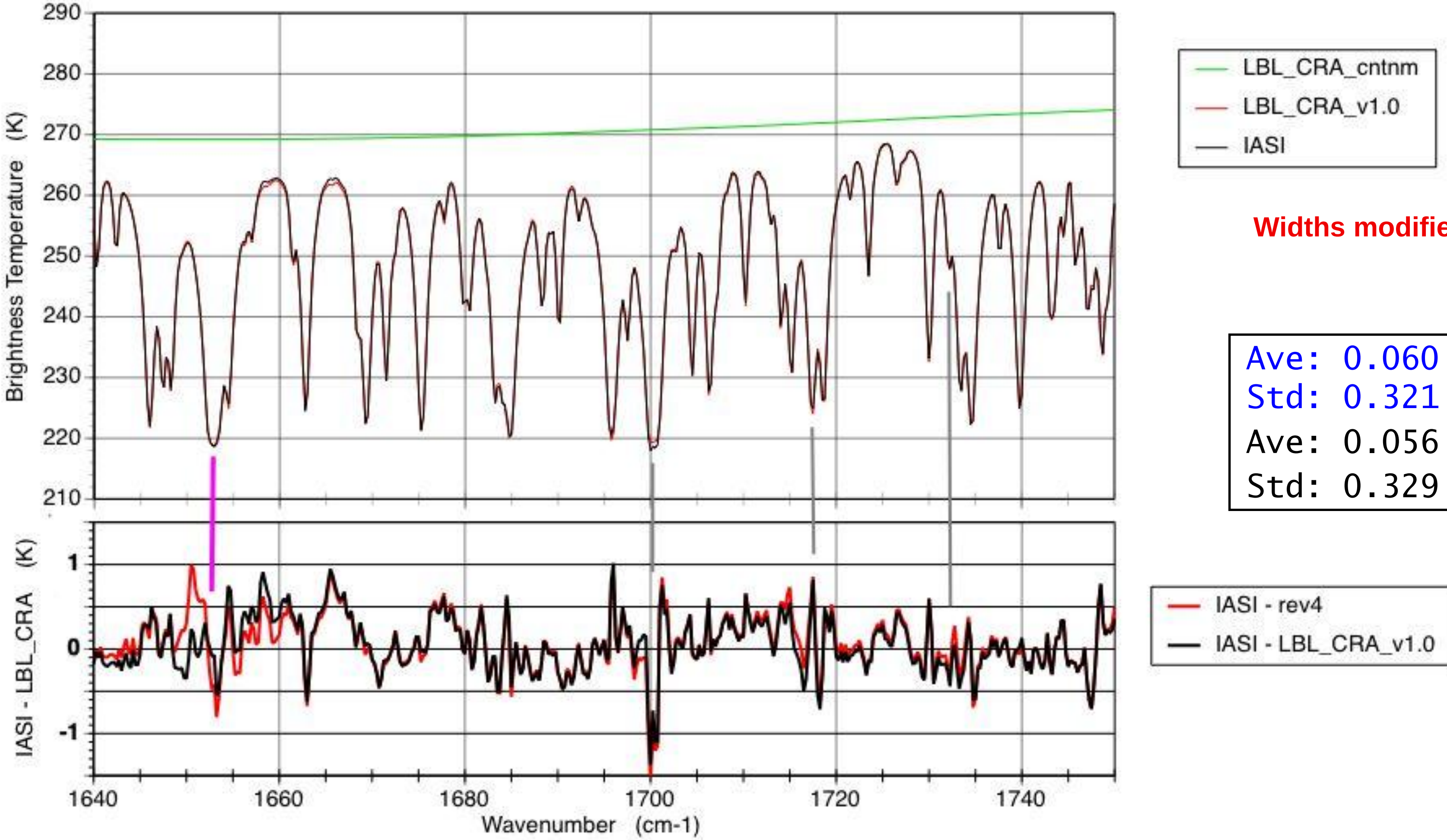
AERI Downwelling Radiances III

ARM NSA Site

PWV: 1.866 mm



Water Vapor R-Branch: 1640 -1750 cm-1



Widths modified

Ave: 0.060 K
Std: 0.321 K
Ave: 0.056 K
Std: 0.329 K

Line Coupling 1653 cm-1