New Measurements of the Water Vapour Continuum

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NATURAL ENVIRONMENT RESEARCH COUNCIL

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Testing the Accuracy of Theoretical Water Vapour Absorption using Laboratory Measurements

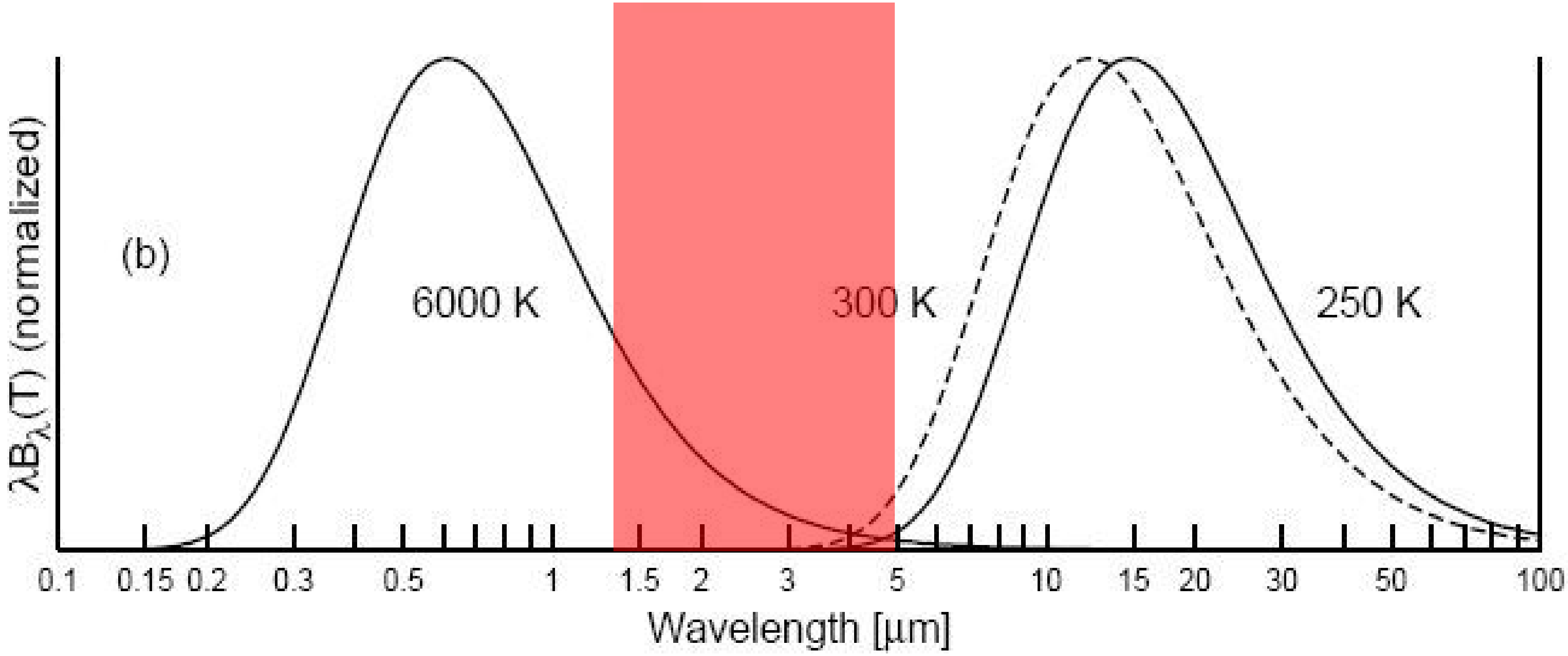
Key Facts:

•Used a FT-IR spectrometer at MSF RAL to measure the absorption of a known amount of **pure** water vapour through a multi-pass cell.

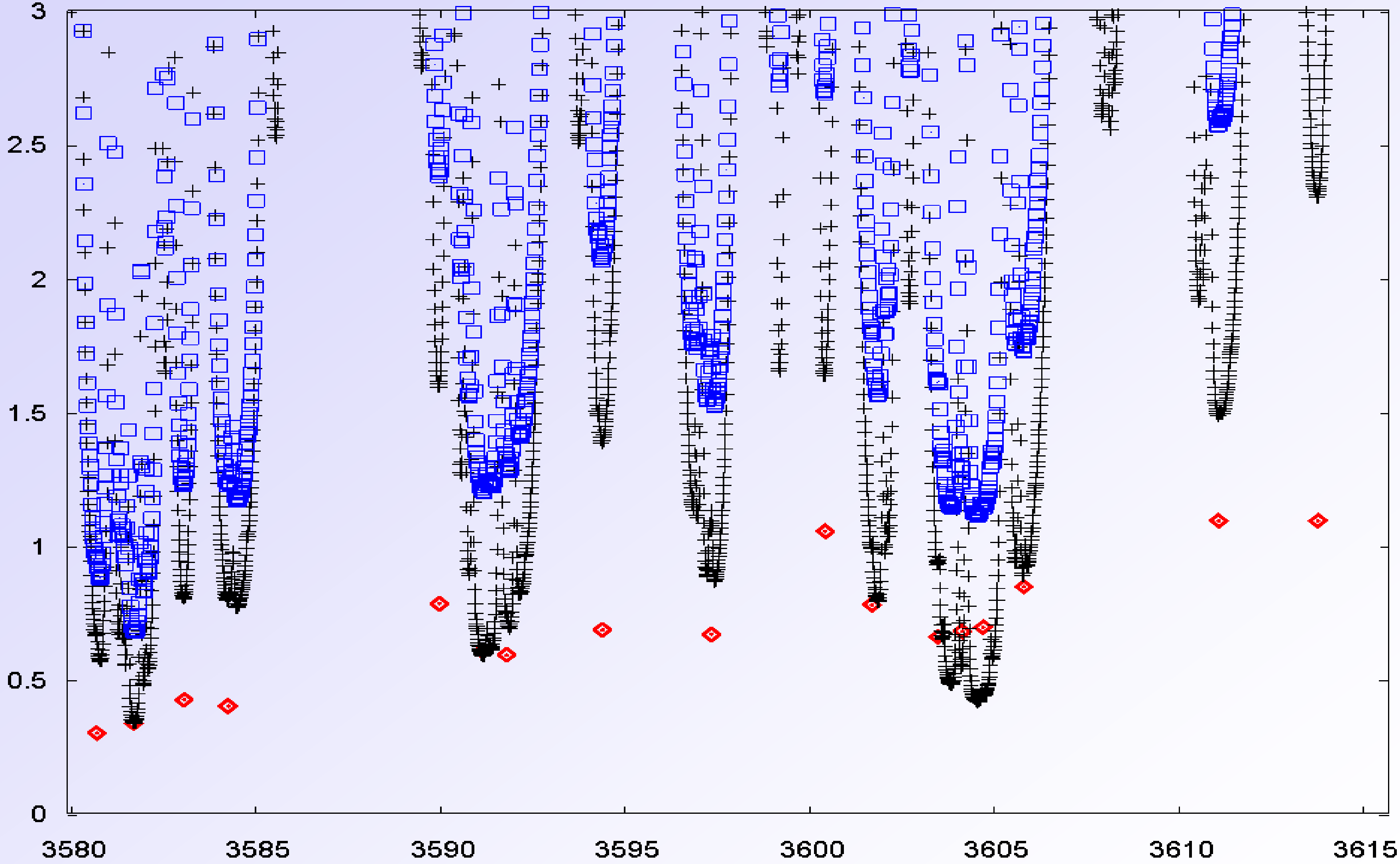
•Measured spectrum between 2000 cm^{-1} and 8000 cm^{-1} (5.00μm – 1.25μm) – Near infrared

• Resolution of 0.03cm^{-1} -No Apodization

Temperature 296-351K Pressure 20mb -350mb



Deriving the Continuum



Theory calculated Using Lorentzian lines out to 25cm^{-1}. Line data from HITRAN 2004

$$\tau_c(v) = \tau_m(v) - \tau_T(v)$$

Water Continuum Theory

The continuum result from binary interactions between water molecules

Possible contributors to the continuum

Far Wings Theory

Adjustments to the Lorentzian Line shape resulting from more accurate modelling of binary collisions

Ma and Tipping (M&T)(2002)

Theoretical

Clough-Kneizys-Davies (CKD) (1989)

Empirical change of individual lines to fit Burch data

Collision Induced Absorption

Collisions cause a change in the dipole moment resulting in additional absorption

Broader absorption lines than normal which increase proportional to vapour pressure squared

Mlawer-Tobin_Clough-Kneizys-Davies (MT_CKD)

Changes of line shape and CIA

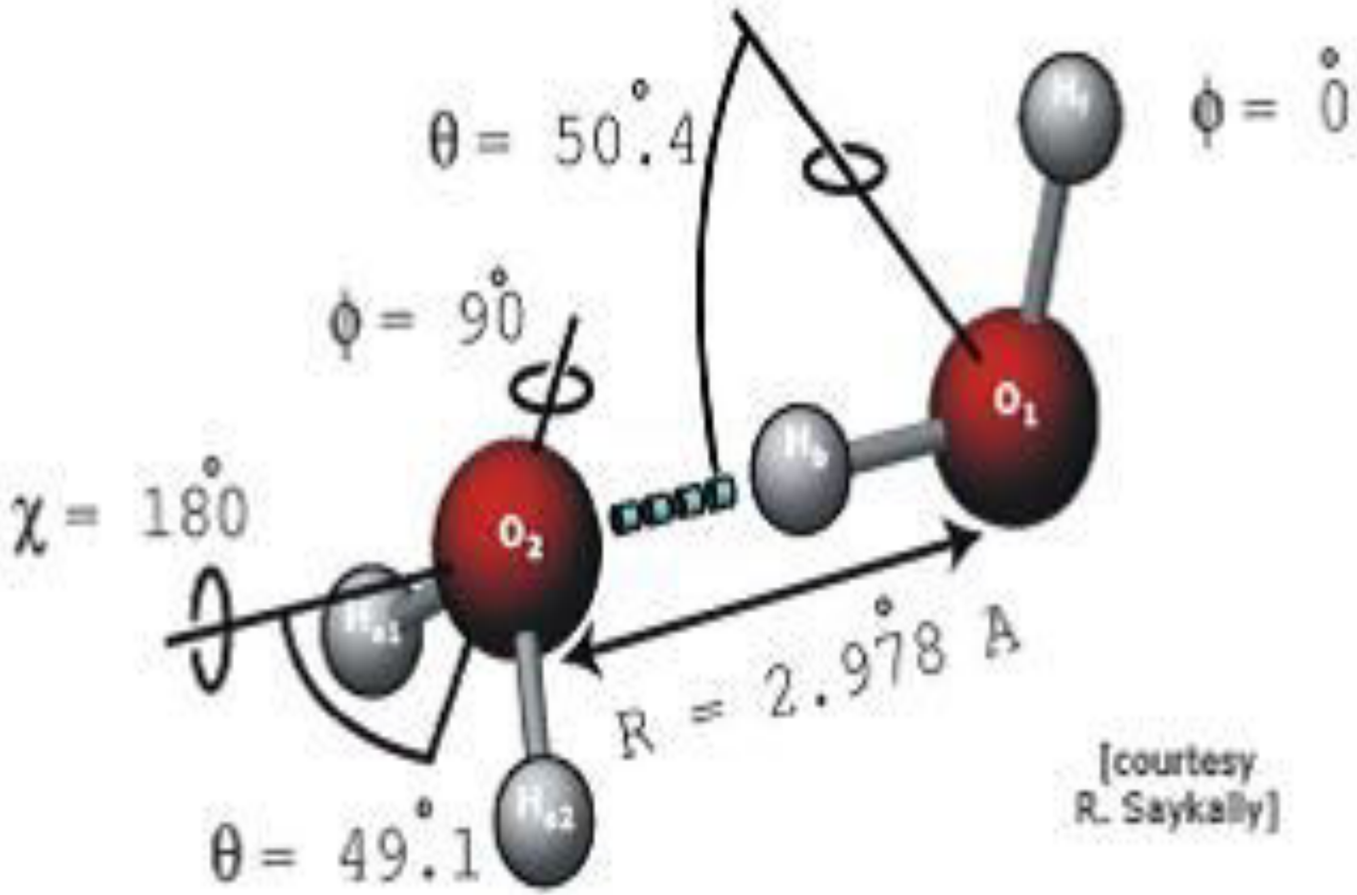
Water Dimer

A hydrogen bond forms between the two water molecules creating a separate absorber.

Exists in both meta-stable and bound states

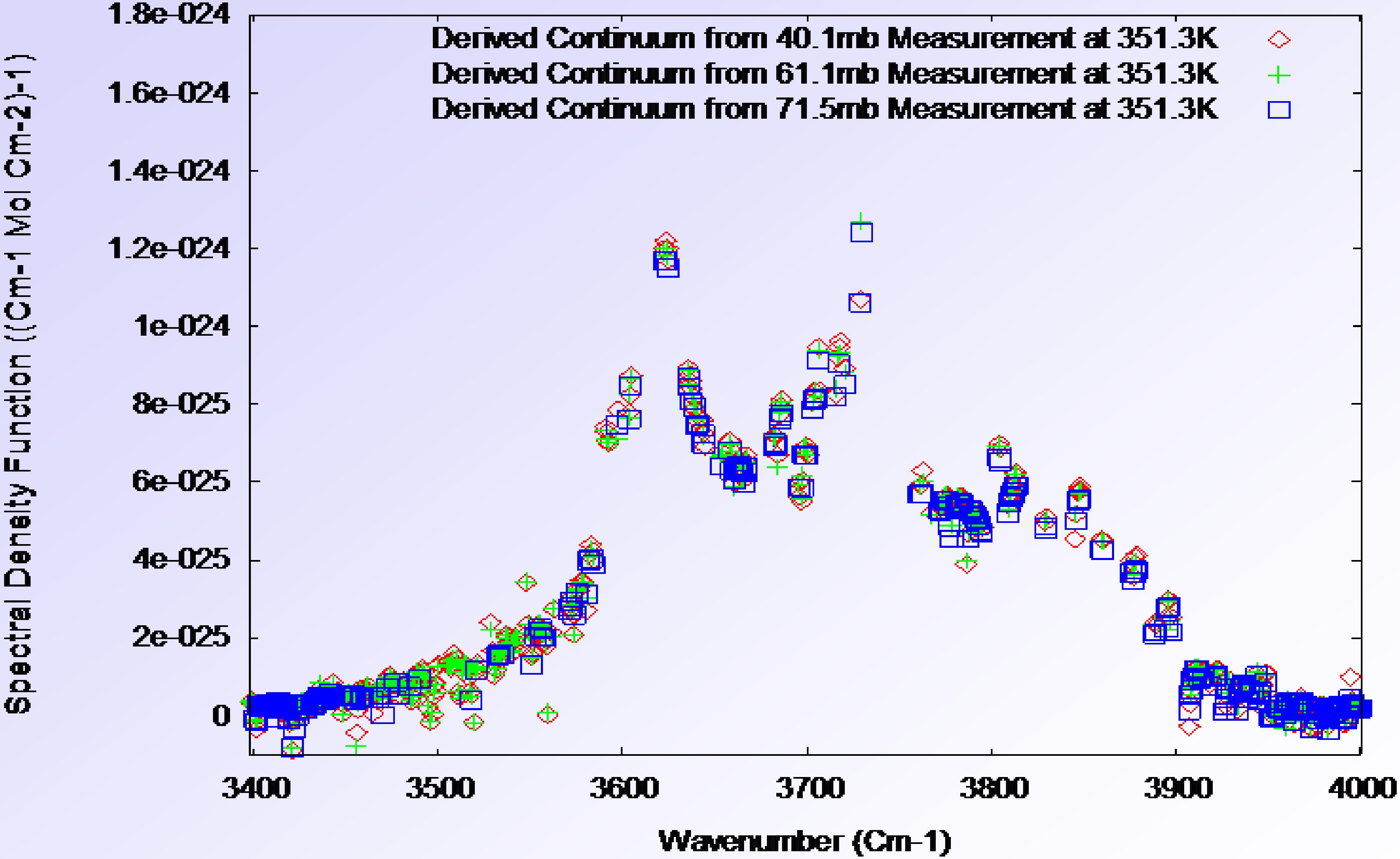
Equilibrium Constant (K_{eq})

Band strengths, position and half widths



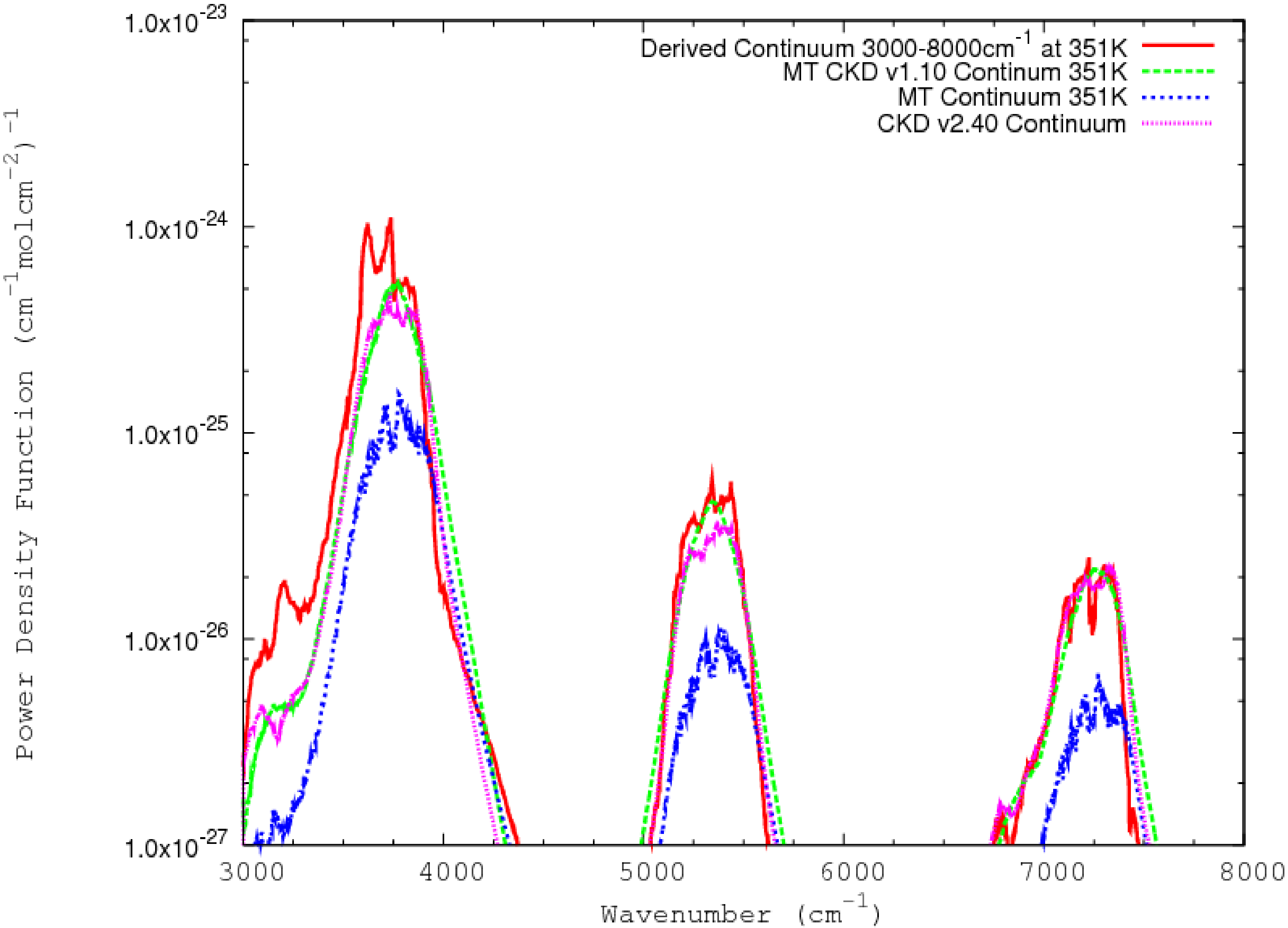
The equilibrium structure of the water dimer as determined by calculations in the VRT(ASP-W) potential surface (Fellers et al., unpublished work). The hydrogen bond deviates 2.3° from linearity, the O-O distance is 2.952 Å, and the bond strength D_0 is 3.4 kcal/mol. The highly non-rigid dimer has six floppy intermolecular vibrations.

Accuracy Test

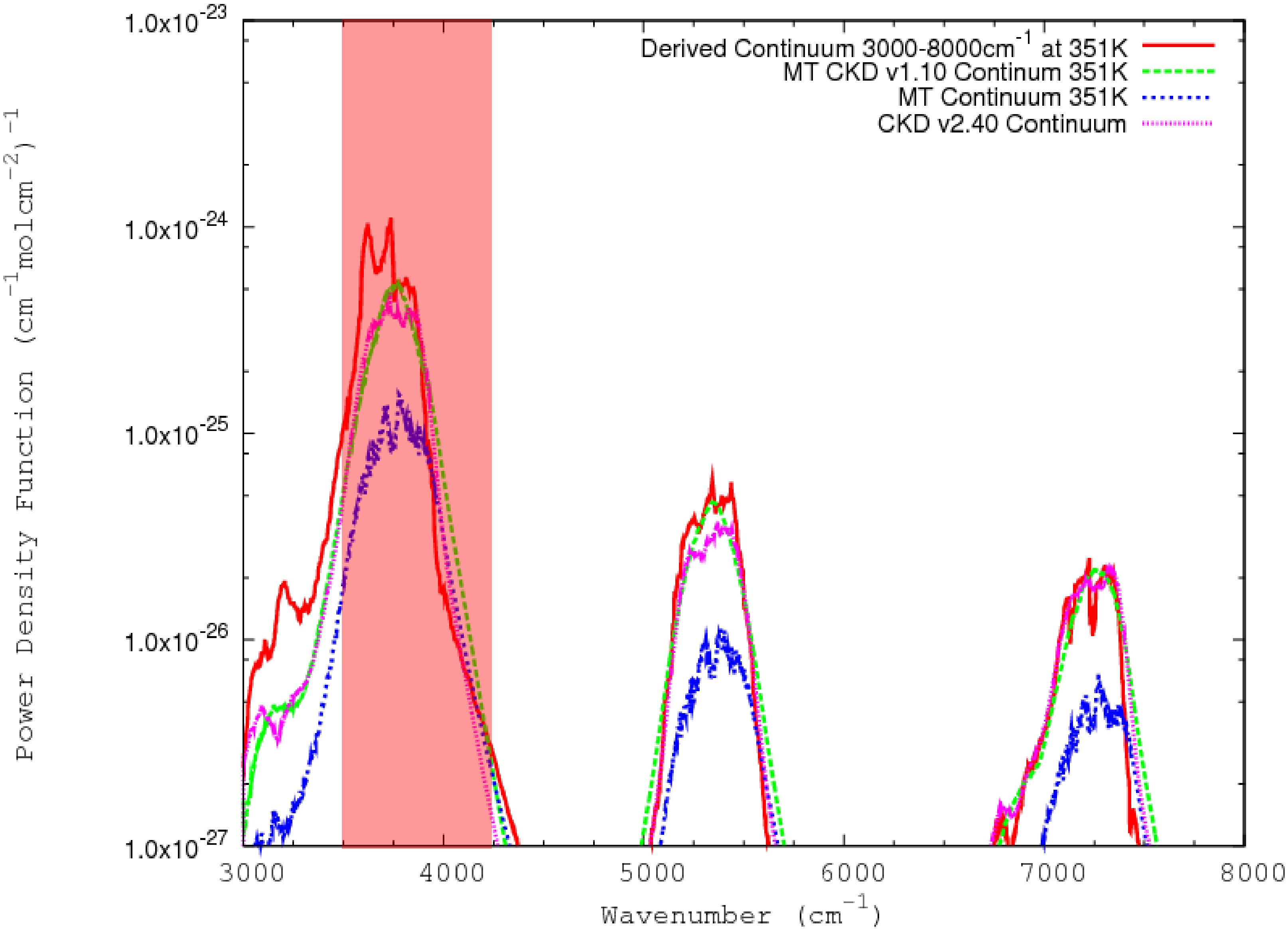


$$C_0(\nu,T)=\frac{k_b T \tau_c}{PL\nu}\left(\frac{P_0}{P}\right)$$

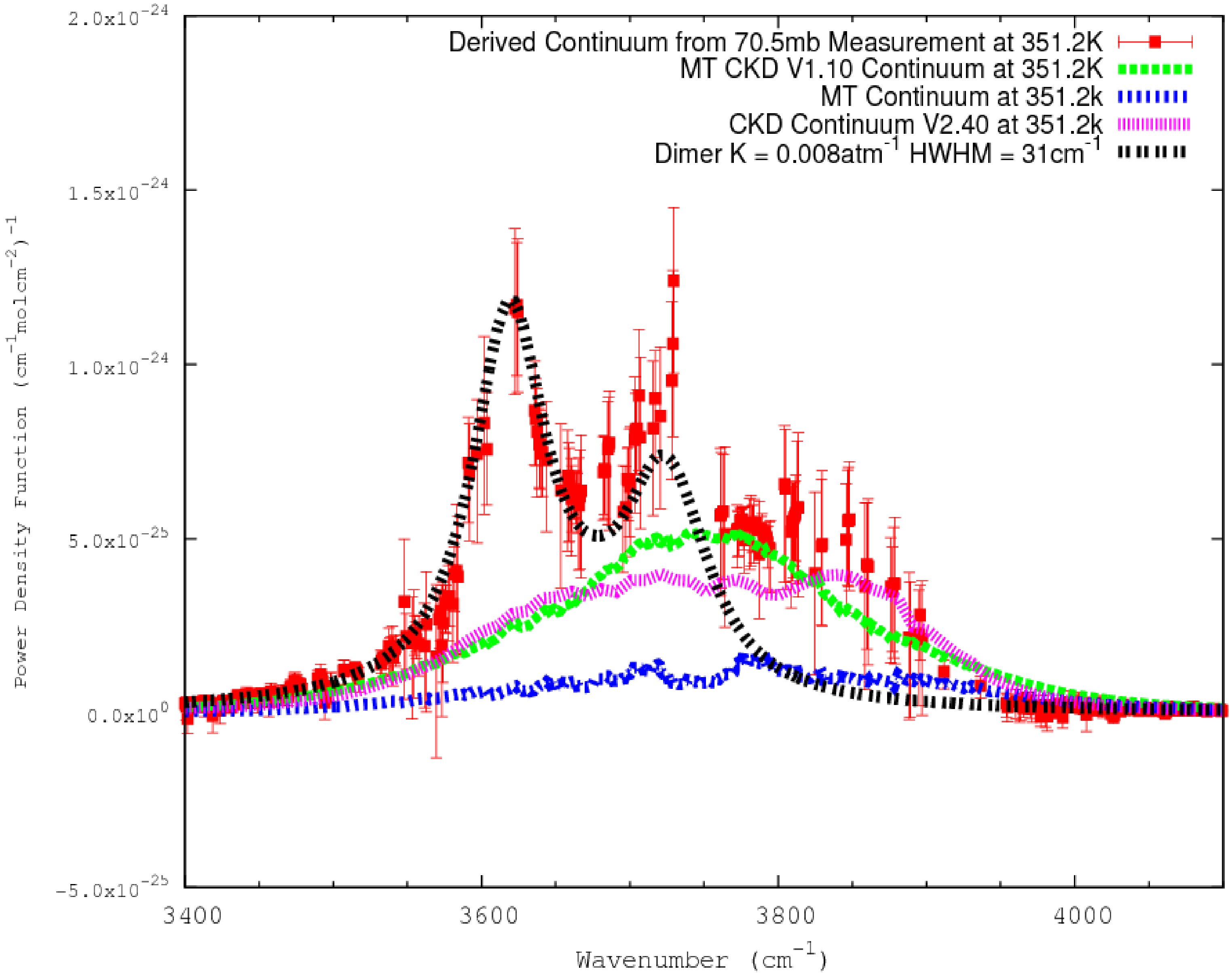
Comparing the Derived Continuum to Theory 3000-8000cm^{-1}(3.3-1.25μm)



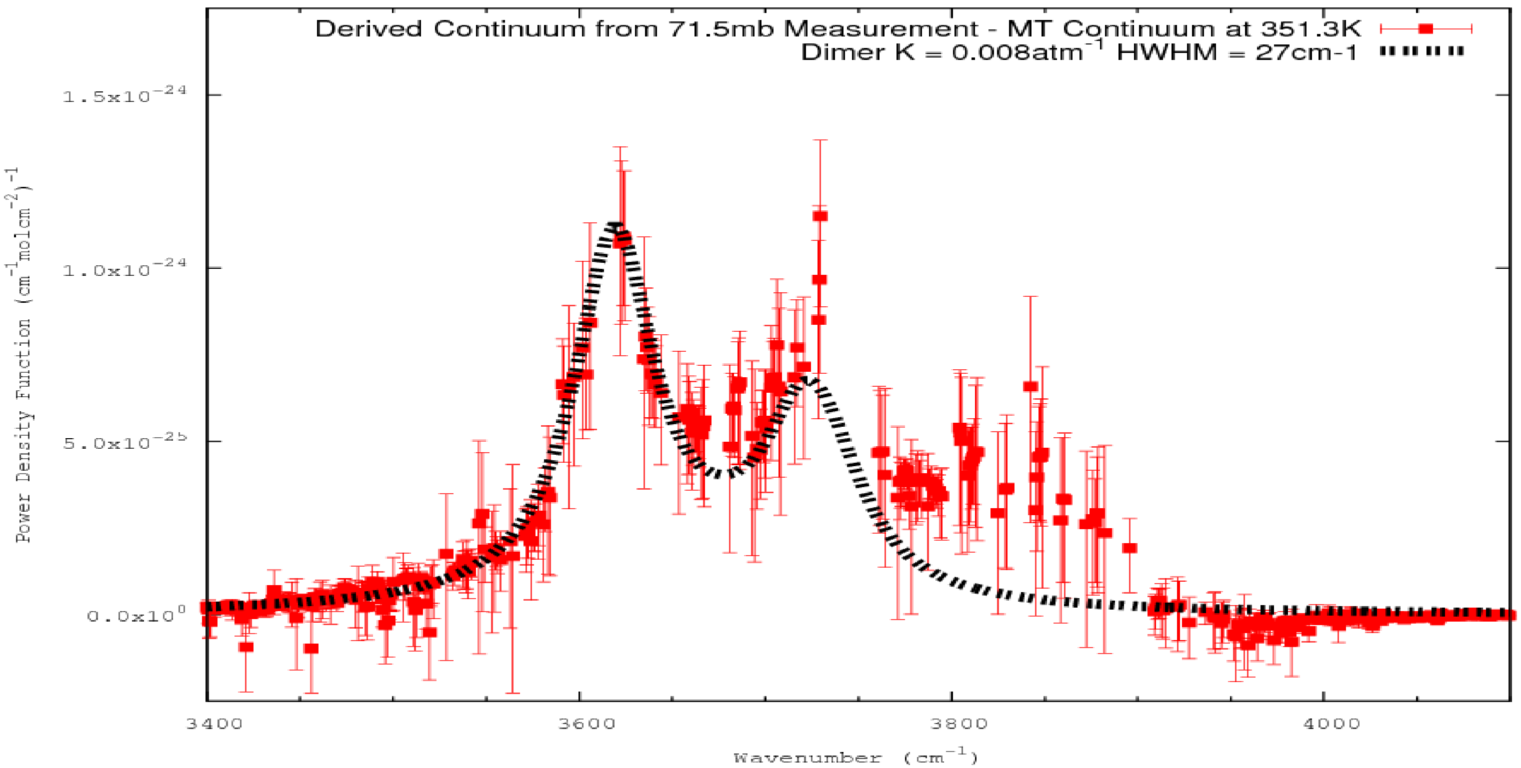
Comparing the Derived Continuum to Theory 3000-8000cm^{-1}(3.3-1.25μm)



Comparing the Derived Continuum to Theory 3400-4200cm^{-1}(3.0-2.4μm)



Fitting Predicted Band Strength of Dimer to Continuum with M&T Continuum Subtracted 3400-4200cm^{-1}(3.0-2.4μm) –Mid Estimate



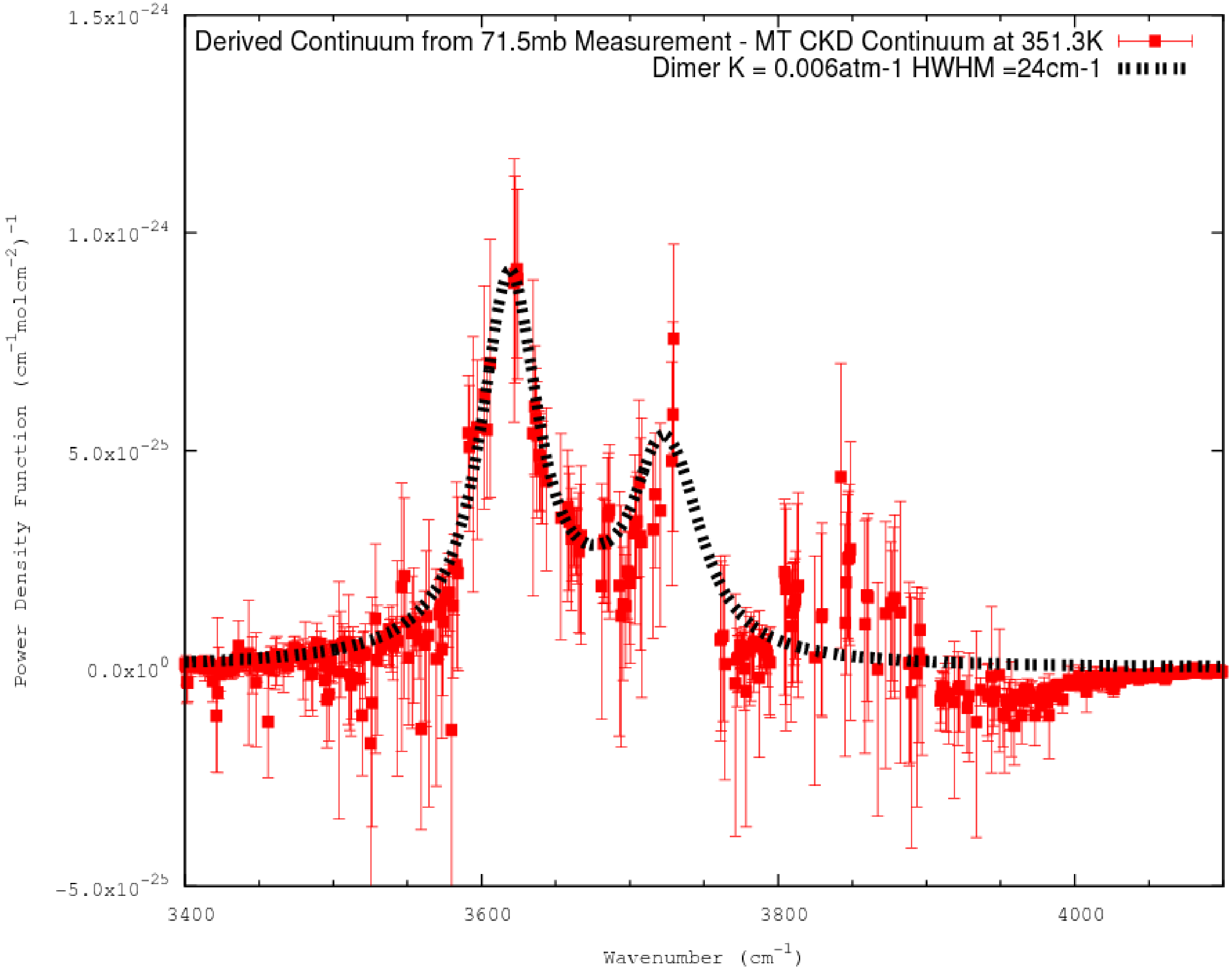
$$C(v,T)_{Dimer} = \frac{K_{eq}(T)}{\pi v} \sum_{i=1..n} S_i \frac{D_i}{(v-v_i)^2 + D_i^2}$$

Dimer Band Strength (S) fitted to *Ab initio* calculations of Schofield and Kjaergaard(2004)

Dimer absorption Proportional

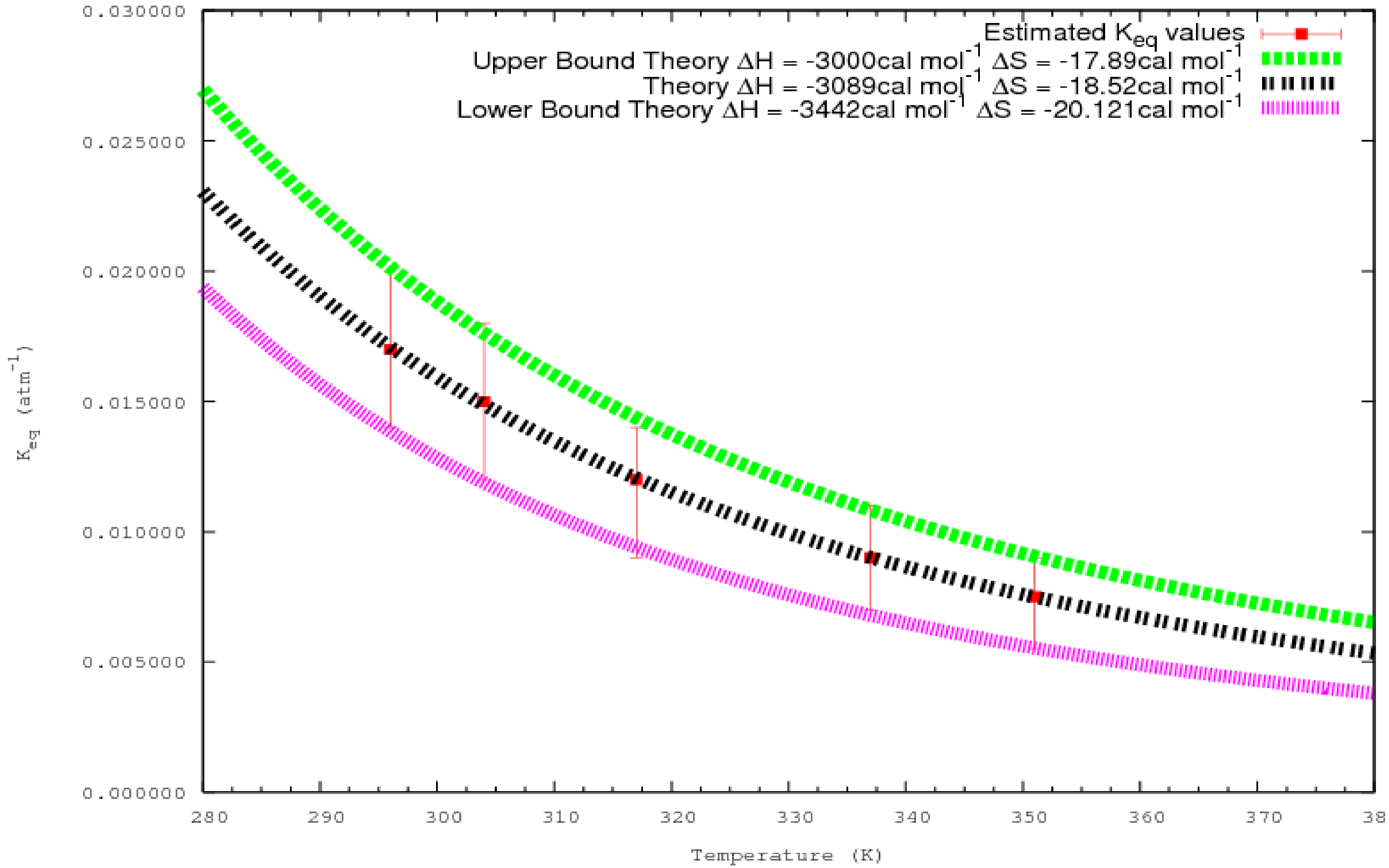
- **Equilibrium constant (Fitted) (K_{eq})**
- **Band Strength S**
- **Band Width D (Fitted)**

Fitting Predicted Band Strength of Dimer to Continuum with MT_CKD Continuum subtracted 3400-4000cm^{-1}(3.0-2.4μm) –Lower Estimate

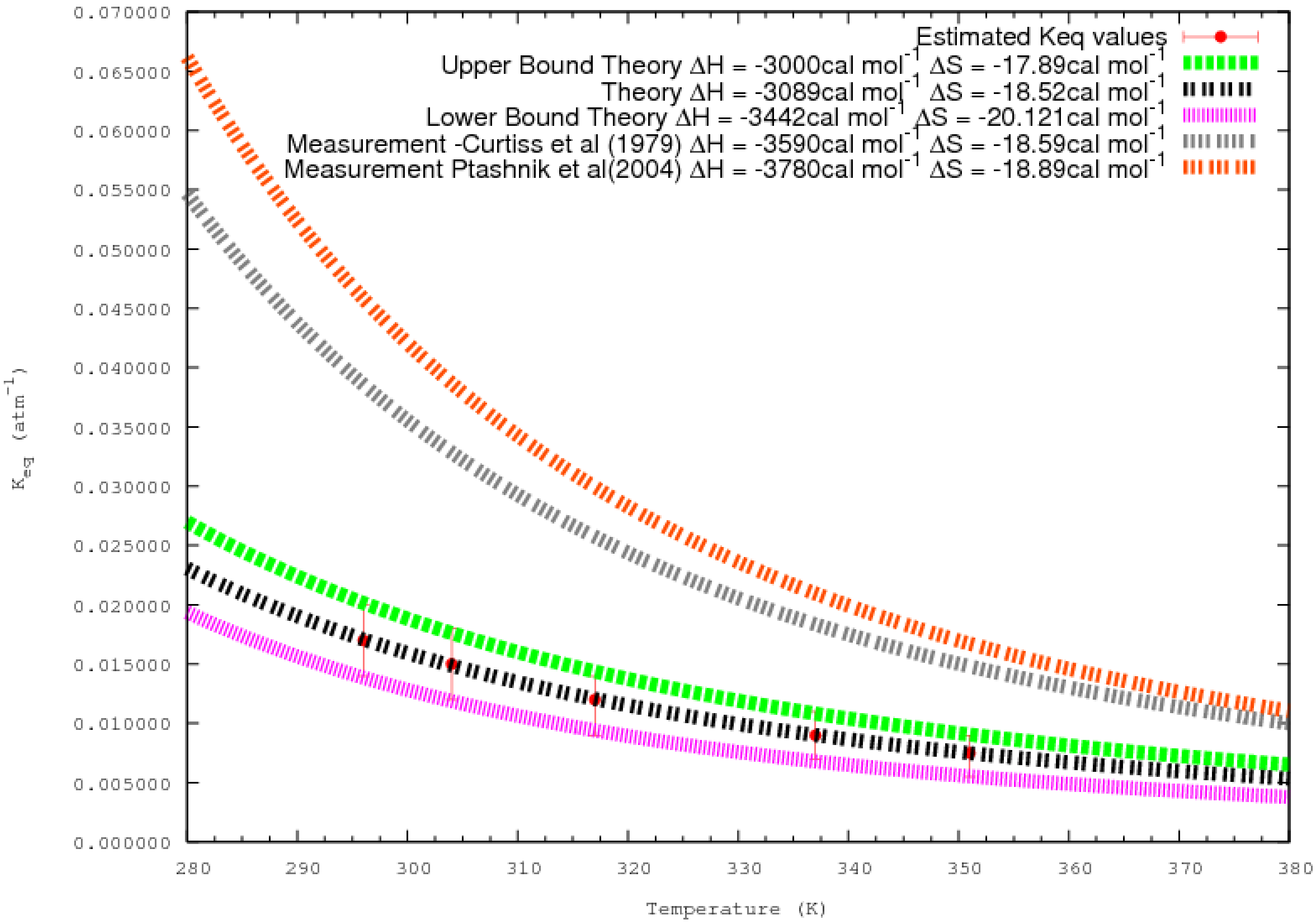


Temperature Dependence of Estimated K_{eq} from 3600cm^{-1} Feature

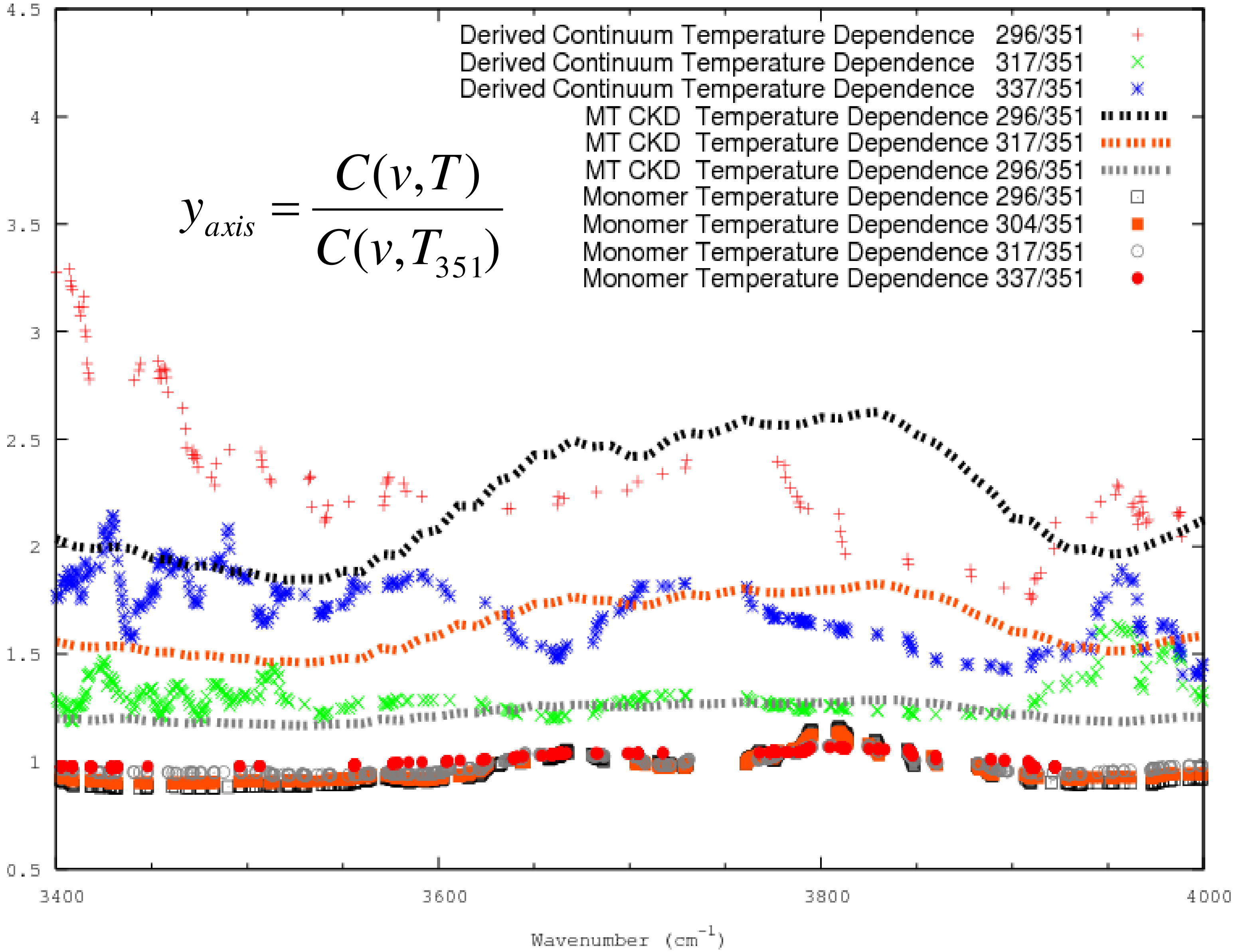
$$K_{eq} = \exp(\Delta S/R - \Delta H/RT)$$



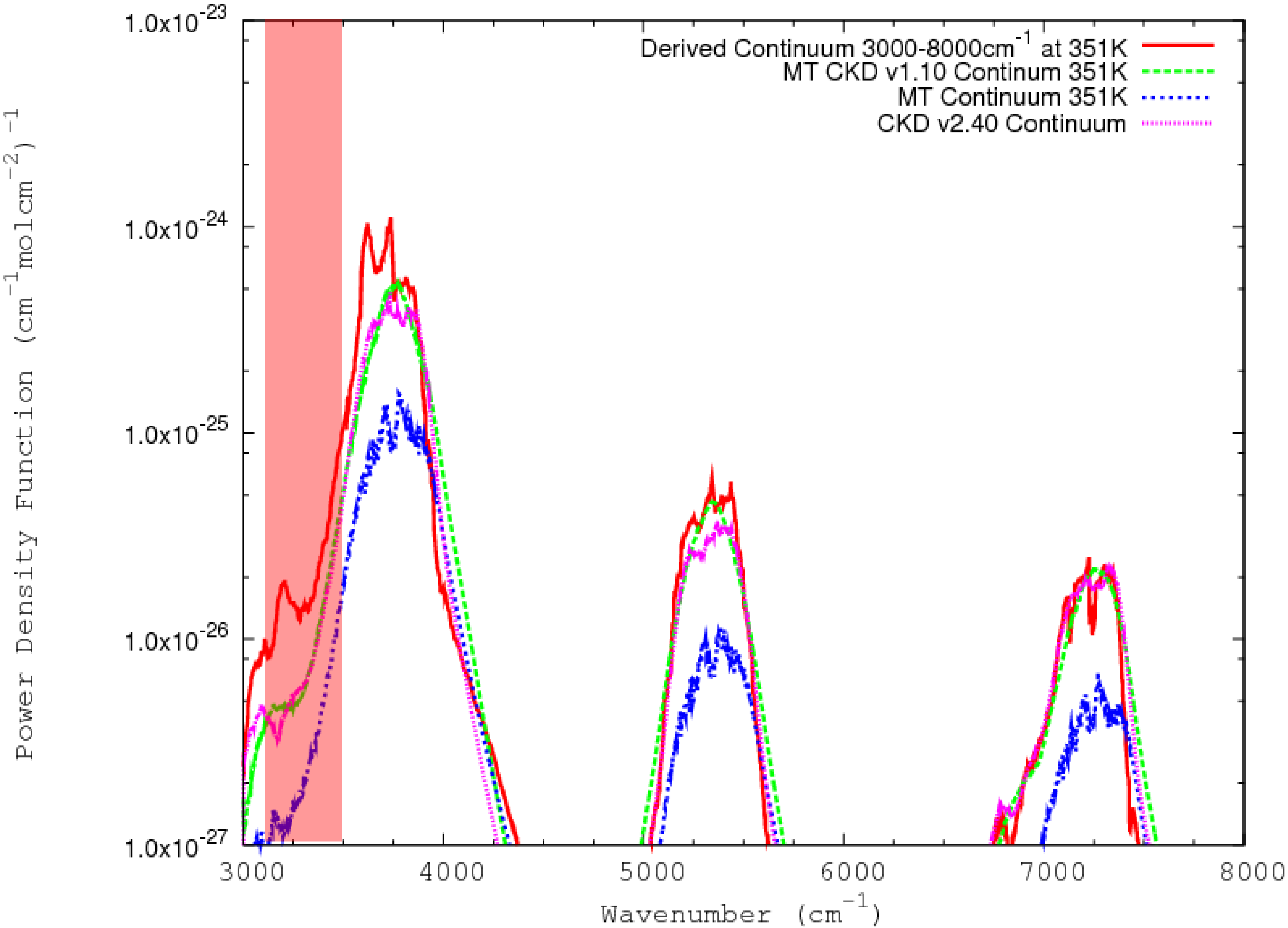
Temperature Dependence of Estimated K_{eq} from 3600cm^{-1} Feature



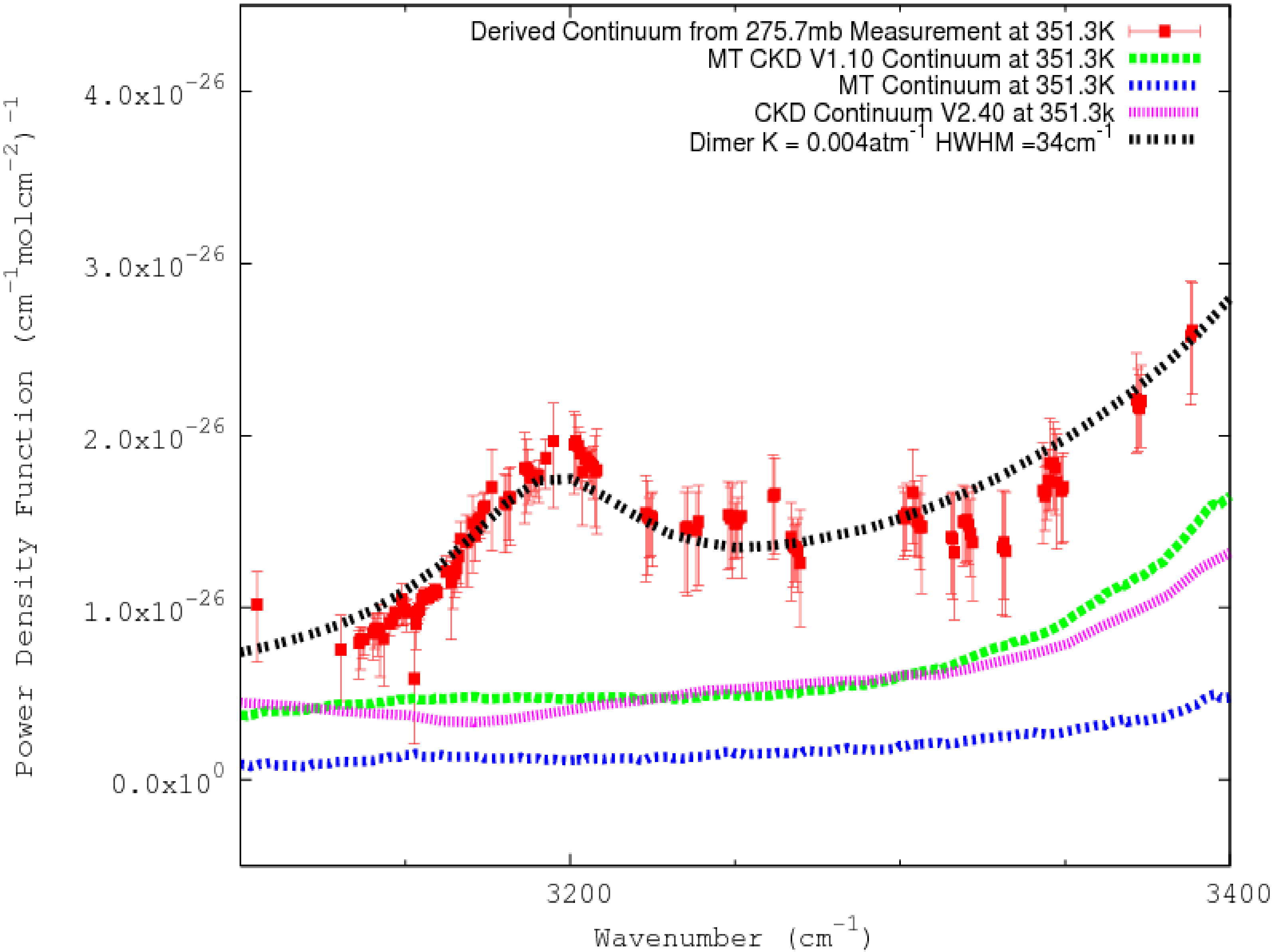
Temperature Dependence of Derived Continuum between 3400-4000cm-1(3.0-2.5μm)



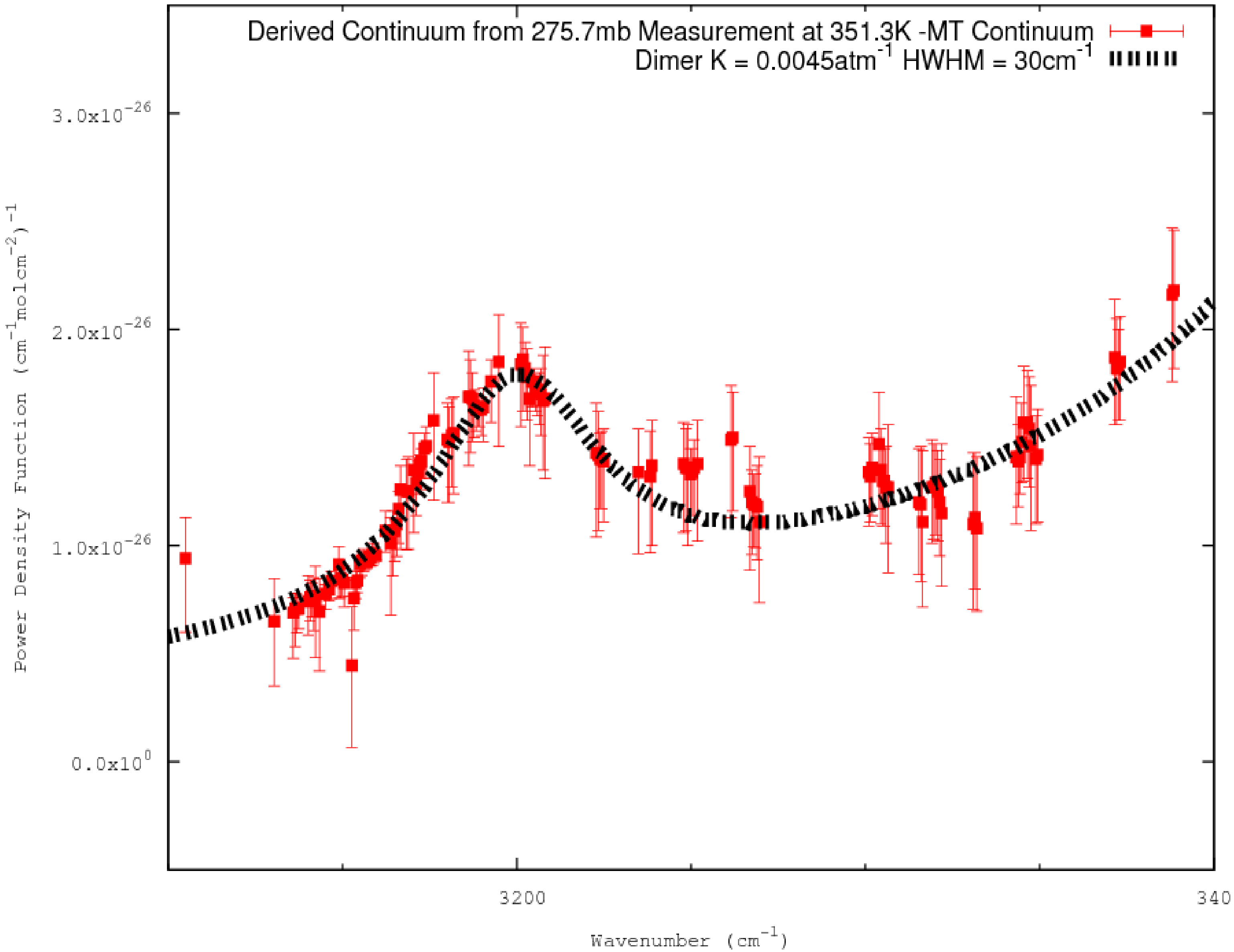
Comparing the Derived Continuum to Theory 3000-8000cm^{-1}(3.0-1.33μm)



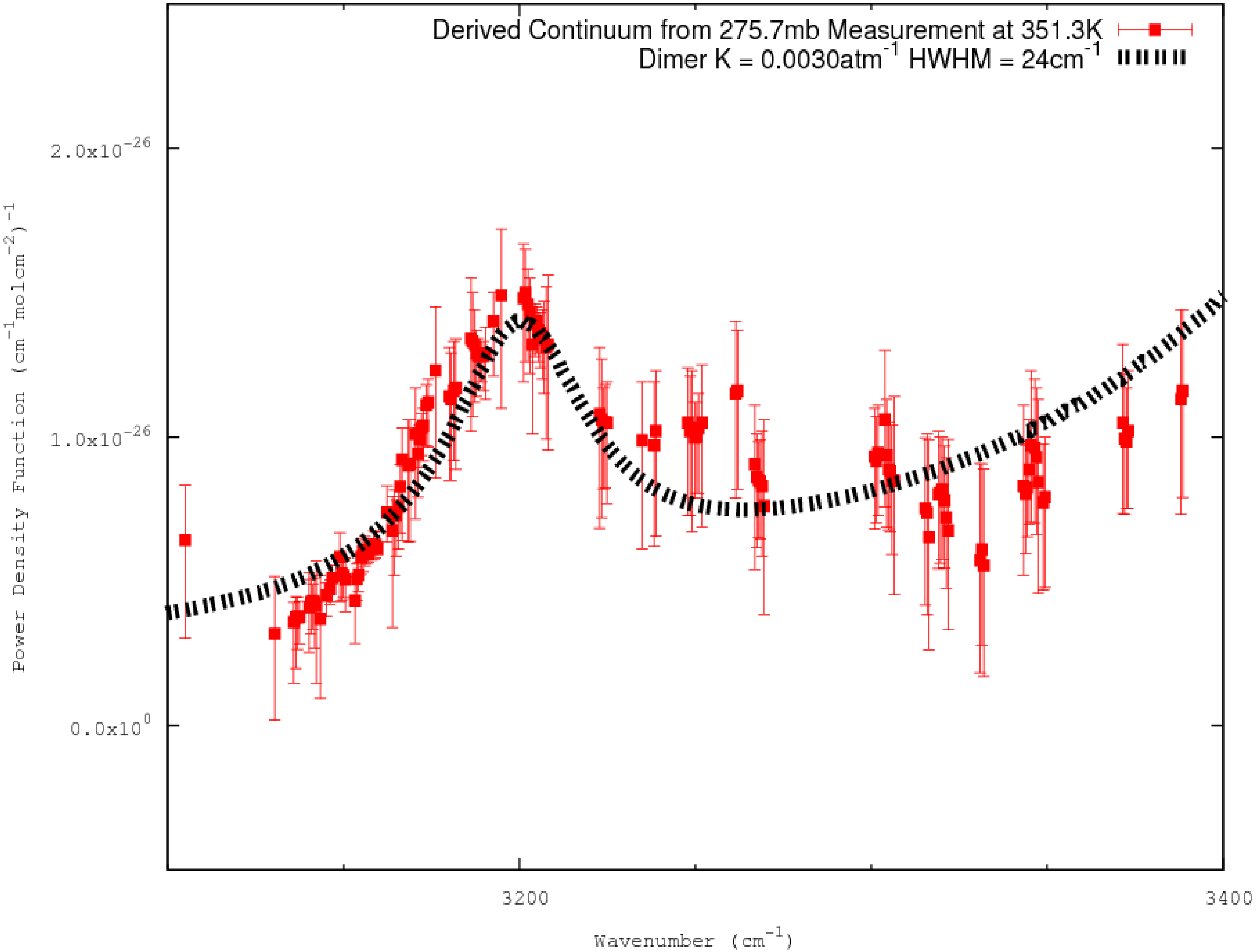
Comparing Derived Continuum to Theory 3100-3400cm-1 (3.2-3.0µm)



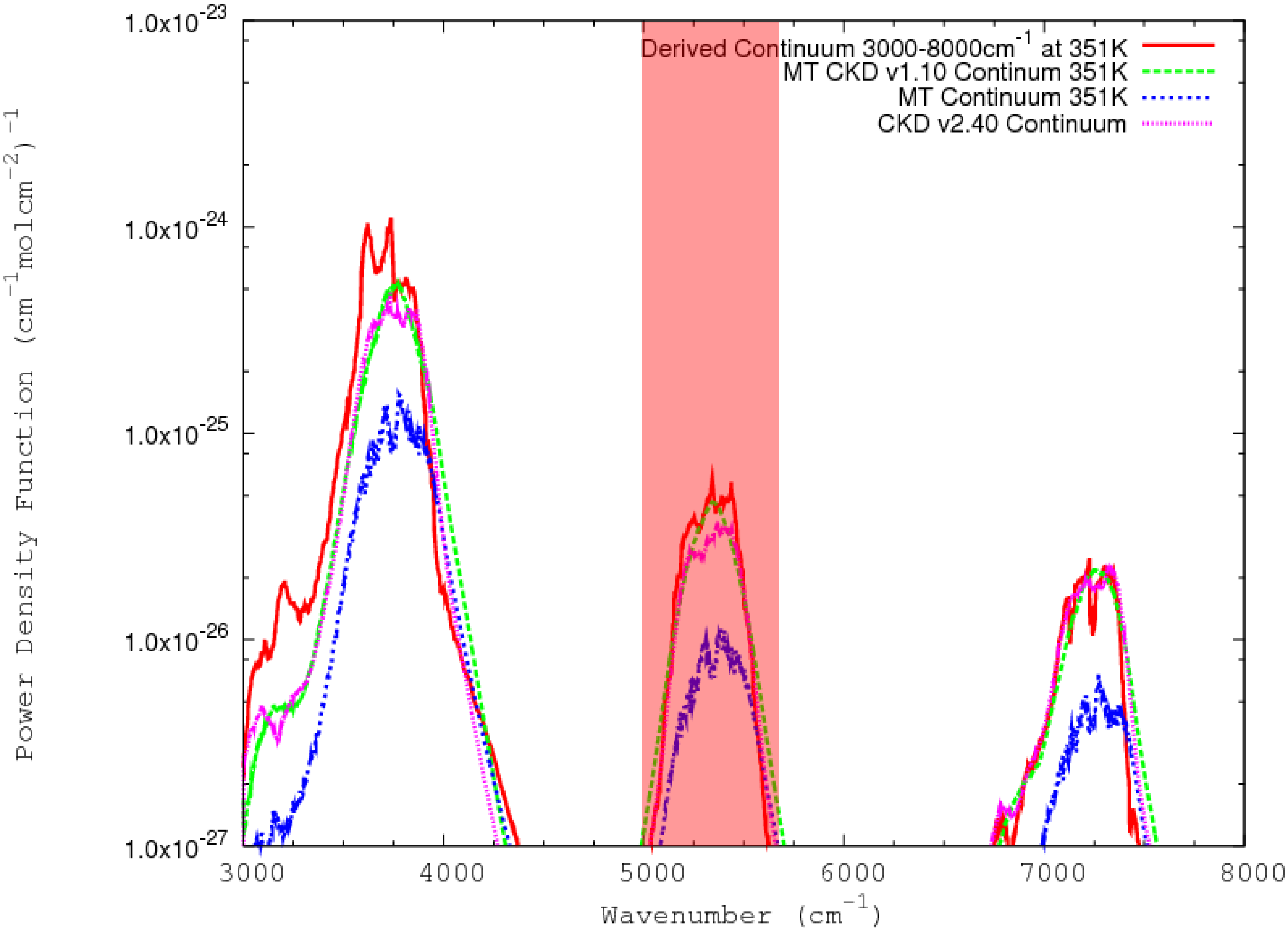
Fitting Predicted Band Strength of Dimer to Continuum with M&T Continuum subtracted 3100-3400cm^{-1} (3.2-3.0μm) – Mid Estimate



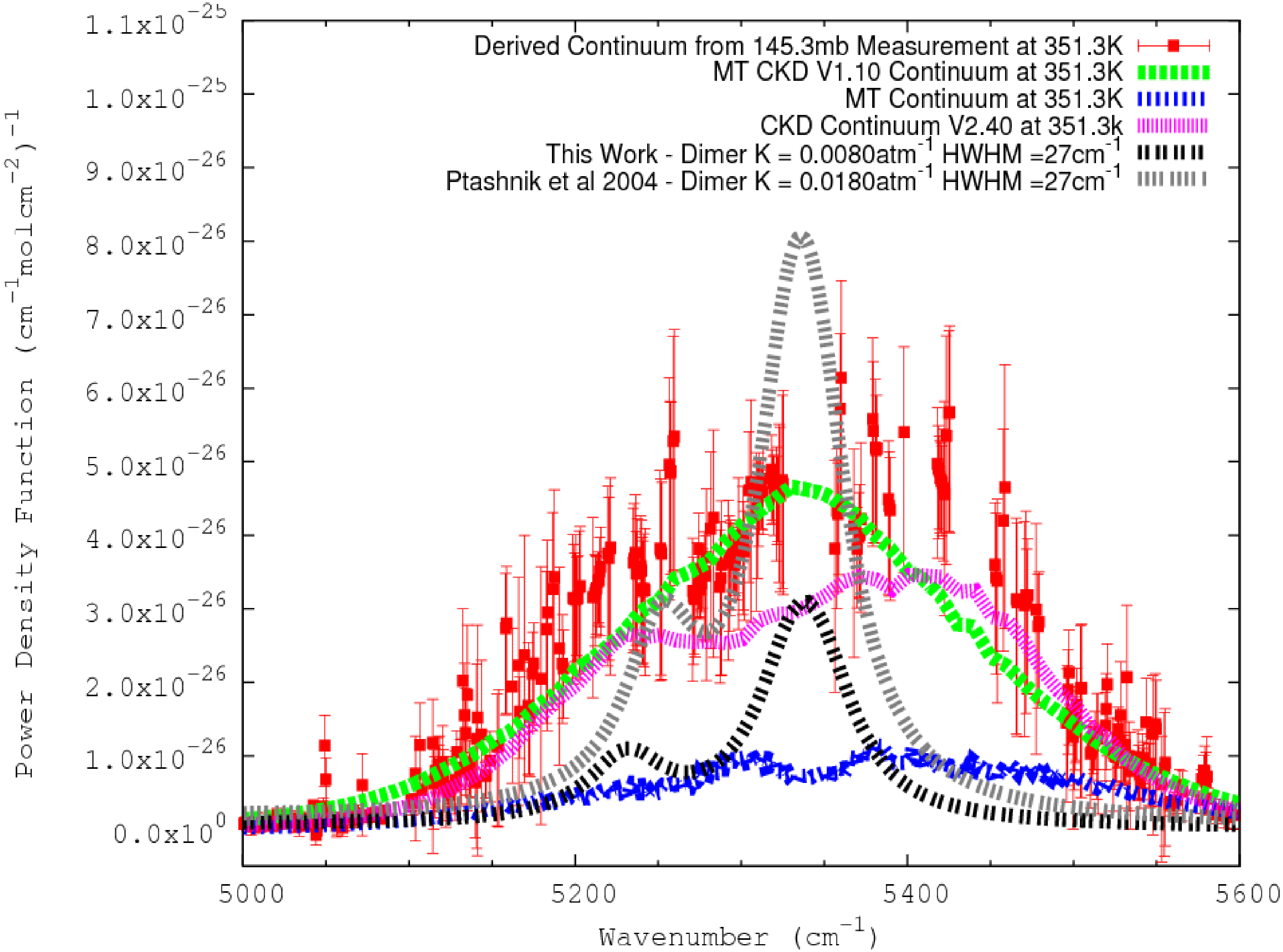
Fitting Predicted Band Strength of Dimer to Continuum with MT_CKD Continuum subtracted 3100-3400cm^{-1} (3.2-3.0μm)- Lower Estimate

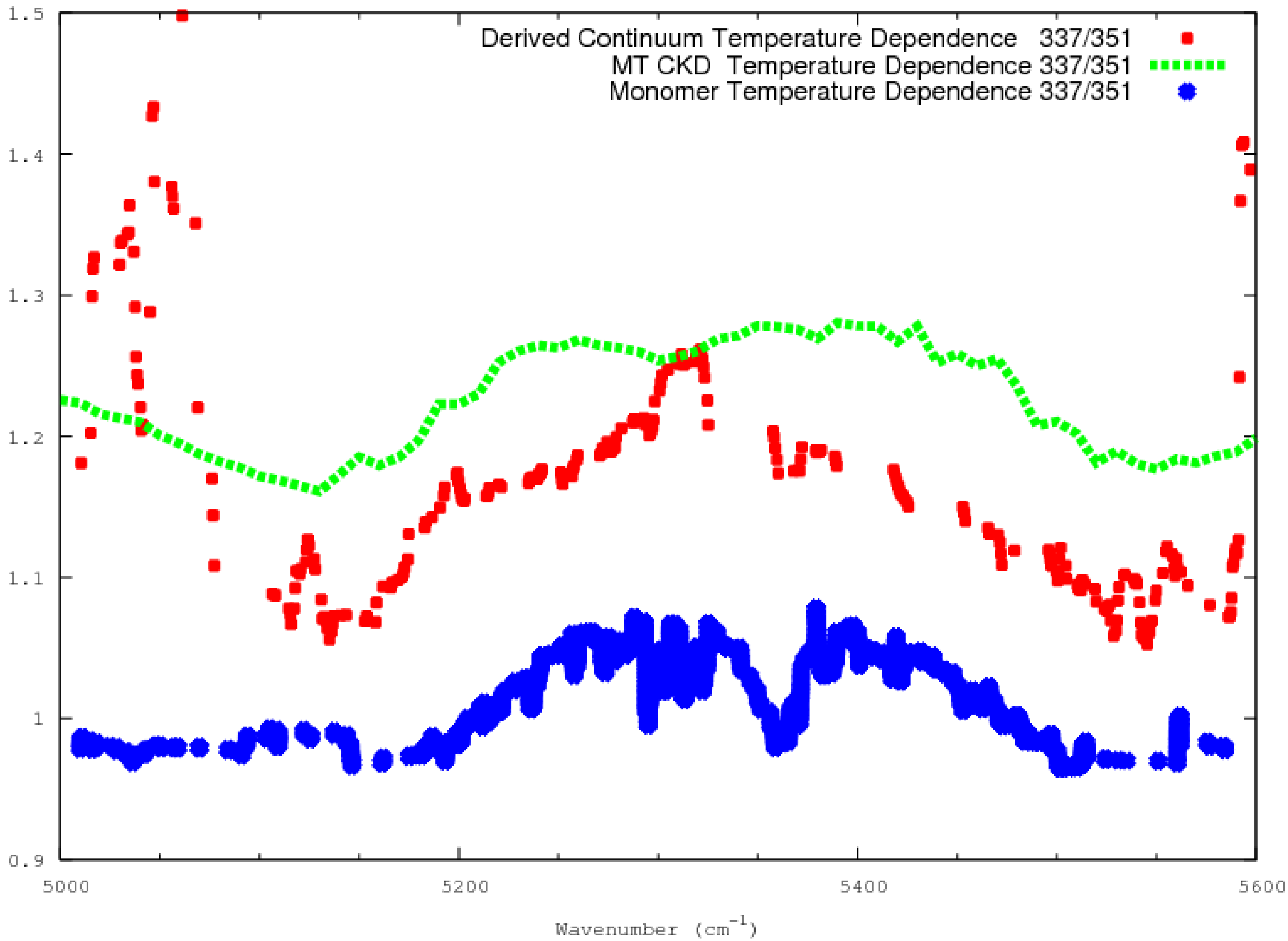


Comparing the Derived Continuum to Theory 3000-8000cm^{-1}(3.0-1.33µm)



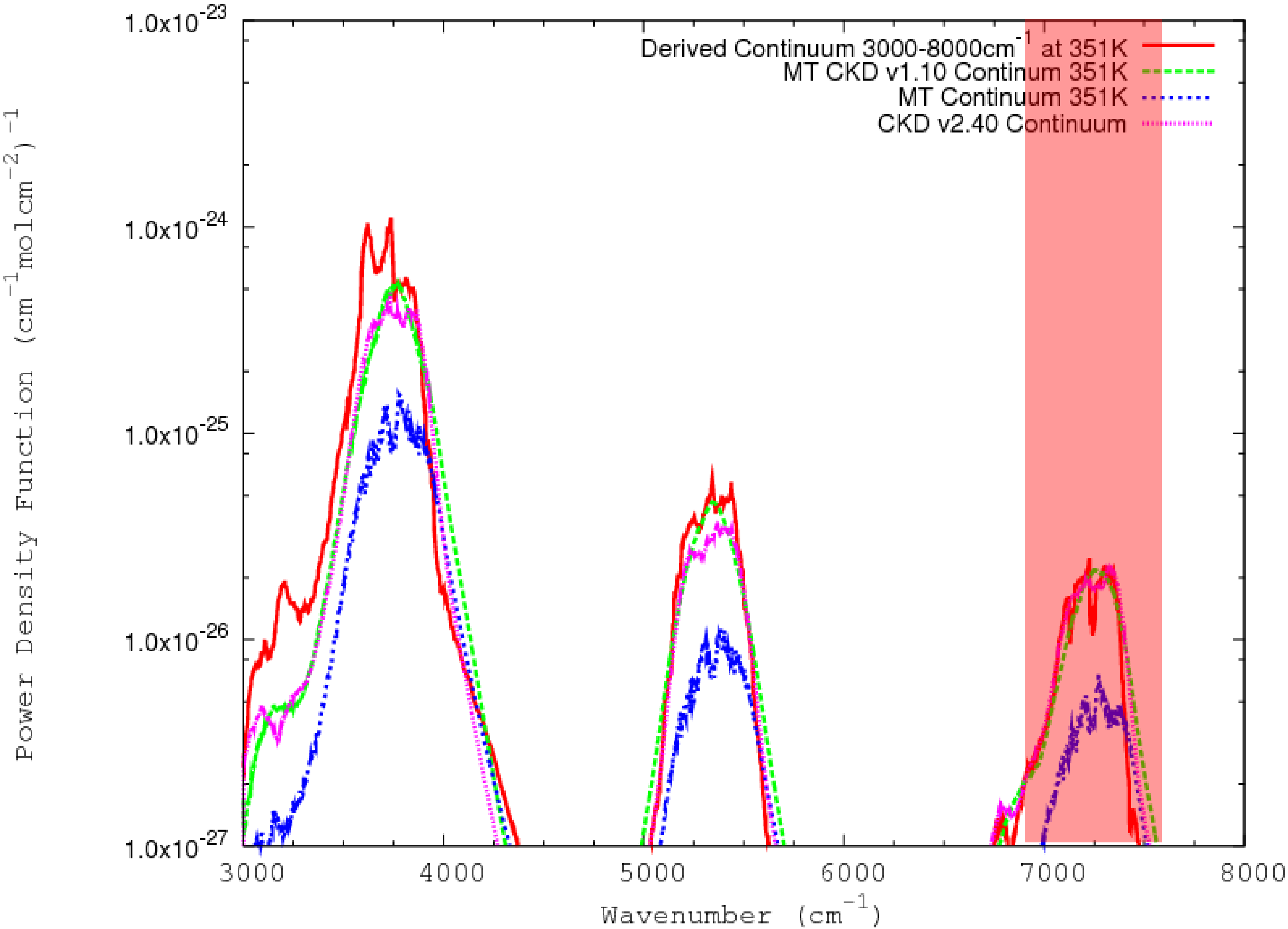
Comparing the Derived Continuum Theory in 5000-5600cm-1 (2.0-1.8μm)



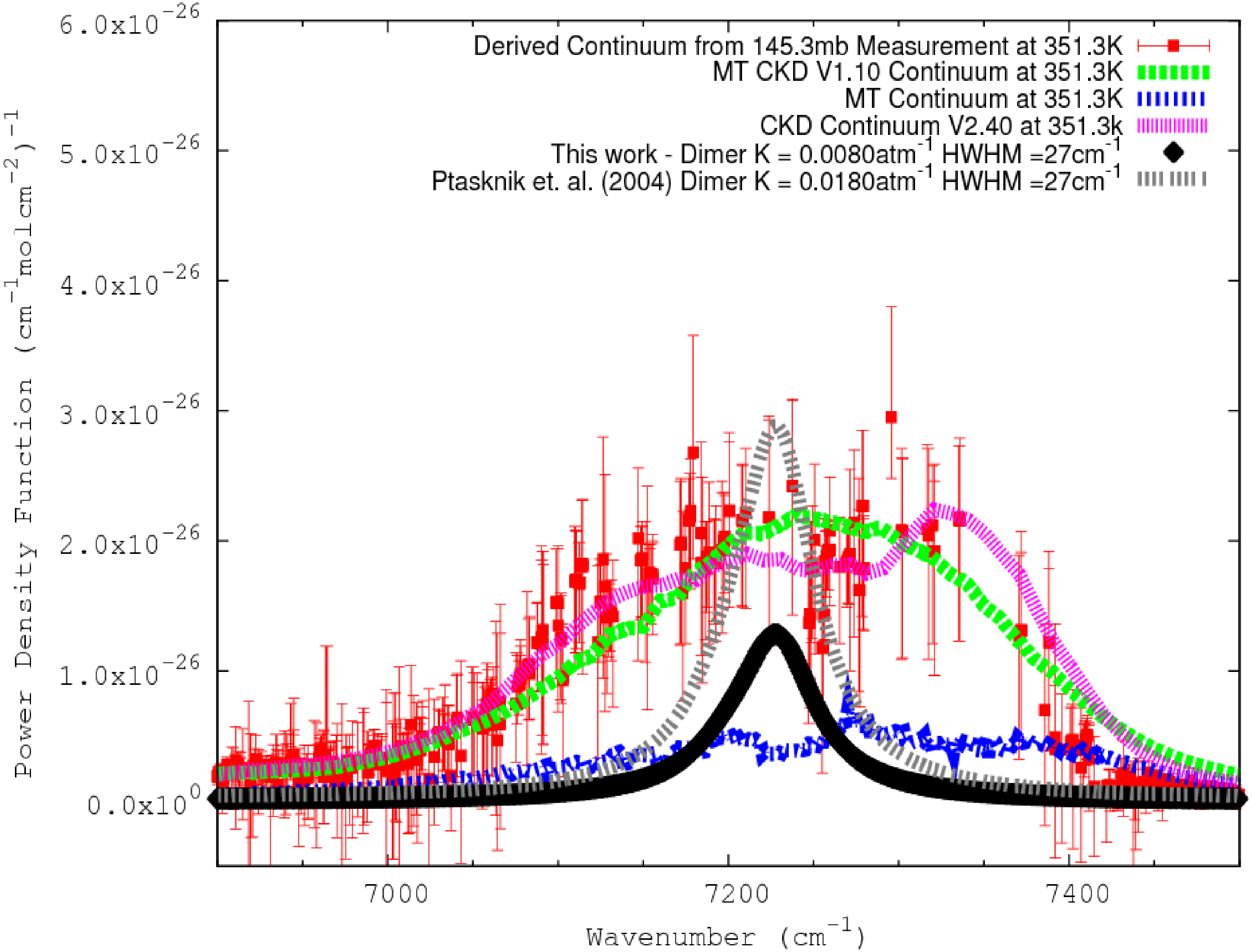


Derived Continuum Temperature Dependence 337/351
MT CKD Temperature Dependence 337/351
Monomer Temperature Dependence 337/351
1.5
1.4
1.3
1.2
1.1
1
0.9
5000
5200
5400
5600
Wavenumber (cm-1)

Comparing the Derived Continuum to Theory 3000-8000cm^{-1}(3.0-1.33μm)



Comparing the Derived Continuum to Theory in 6900-7500cm-1(1.45-1.33μm)



Summary

•Pure water vapour continuum derived between 3000 and 8000 cm^{-1} using HITRAN 2004

•M&T alone underestimates the continuum in all regions

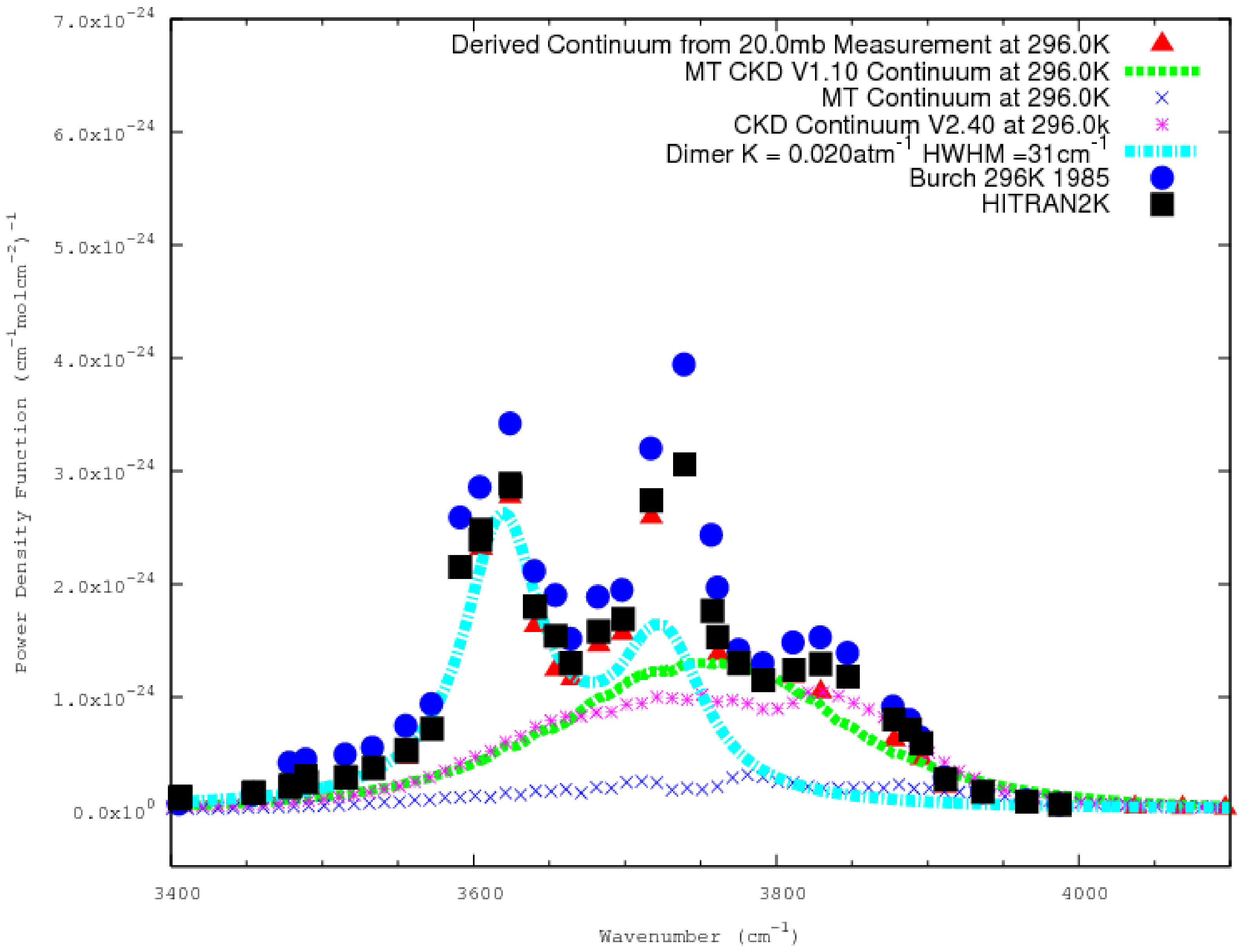
•MT_CKD estimates continuum well in 5000 cm^{-1} and 8000 cm^{-1} regions

•3000-4000 cm^{-1} regions has features not captured by any continuum models

•Possible dimer features at 3200 cm^{-1} and 3600 cm^{-1} Uncertainties in Band Strength and K_{eq}

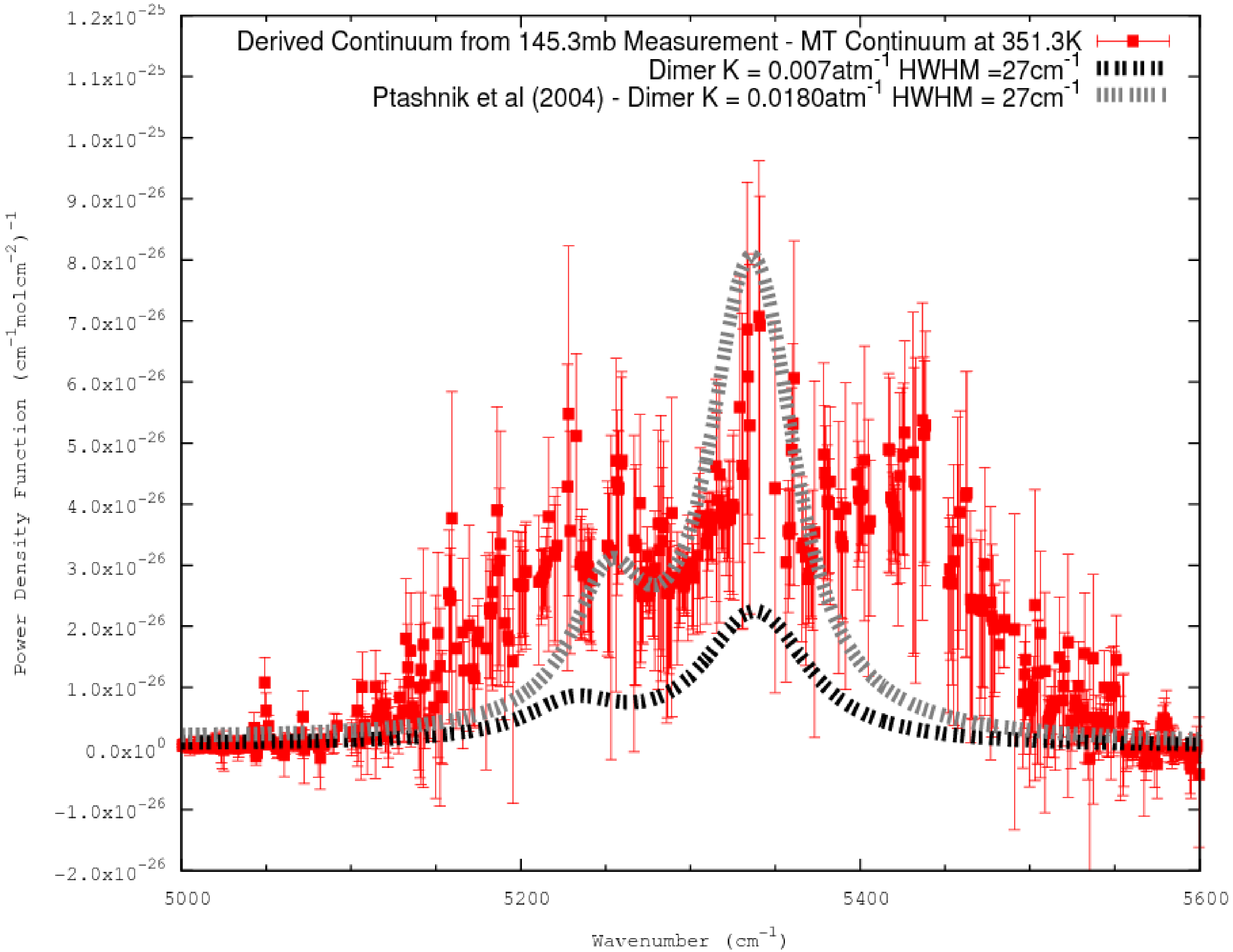
•MT_CKD Temperature dependence generally accurate


Any Questions??

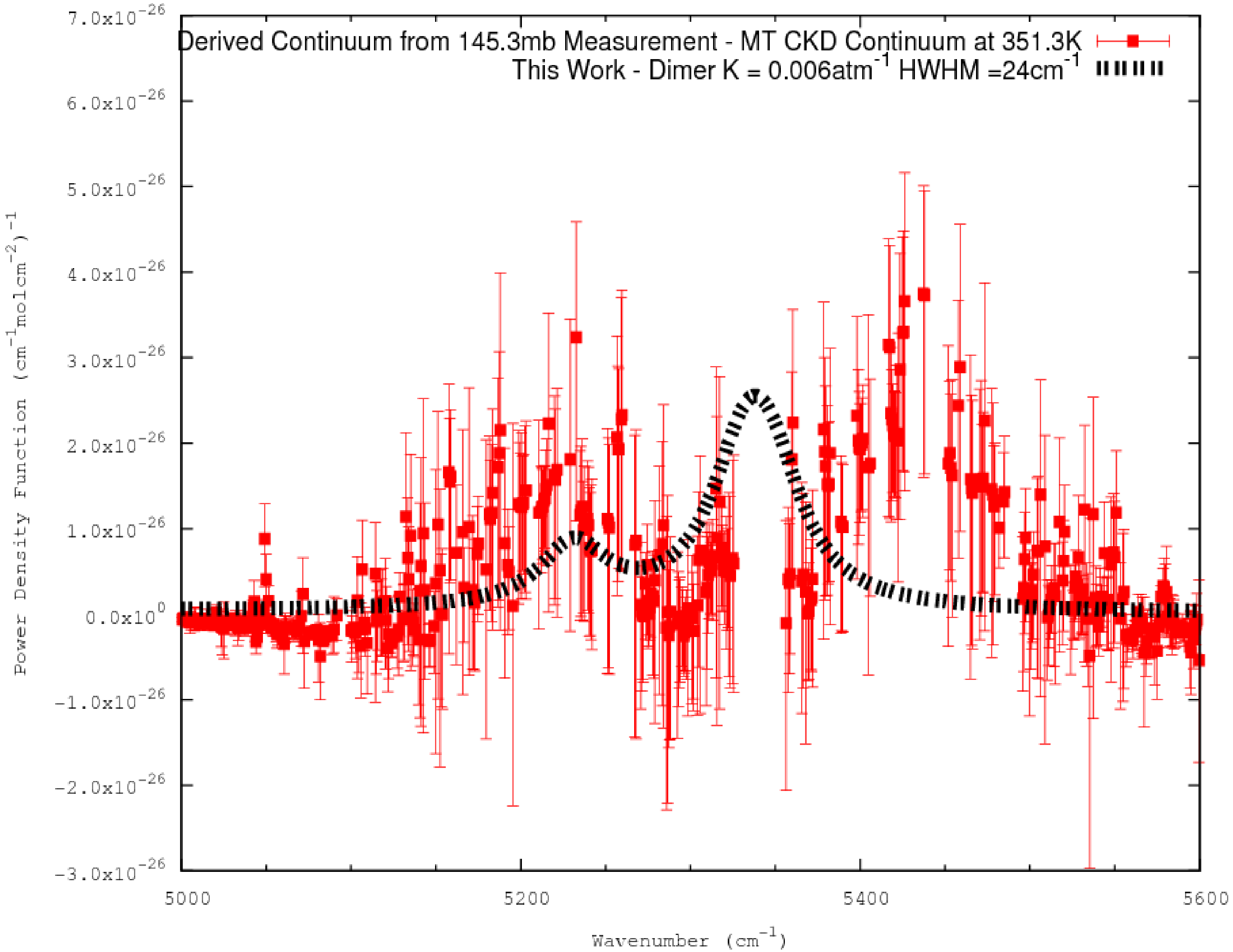


Derived Continuum from 20.0mb Measurement at 296.0K
MT CKD V1.10 Continuum at 296.0K
MT Continuum at 296.0K
CKD Continuum V2.40 at 296.0k
Dimer K = 0.020atm^-1 HWHM =31cm^-1
Burch 296K 1985
HITRAN2K
7.0x10^-24
6.0x10^-24
5.0x10^-24
4.0x10^-24
3.0x10^-24
2.0x10^-24
1.0x10^-24
0.0x10^0
Power Density Function (cm^-1 molcm^-2)^-1
3400
3600
3800
4000
Wavenumber (cm^-1)

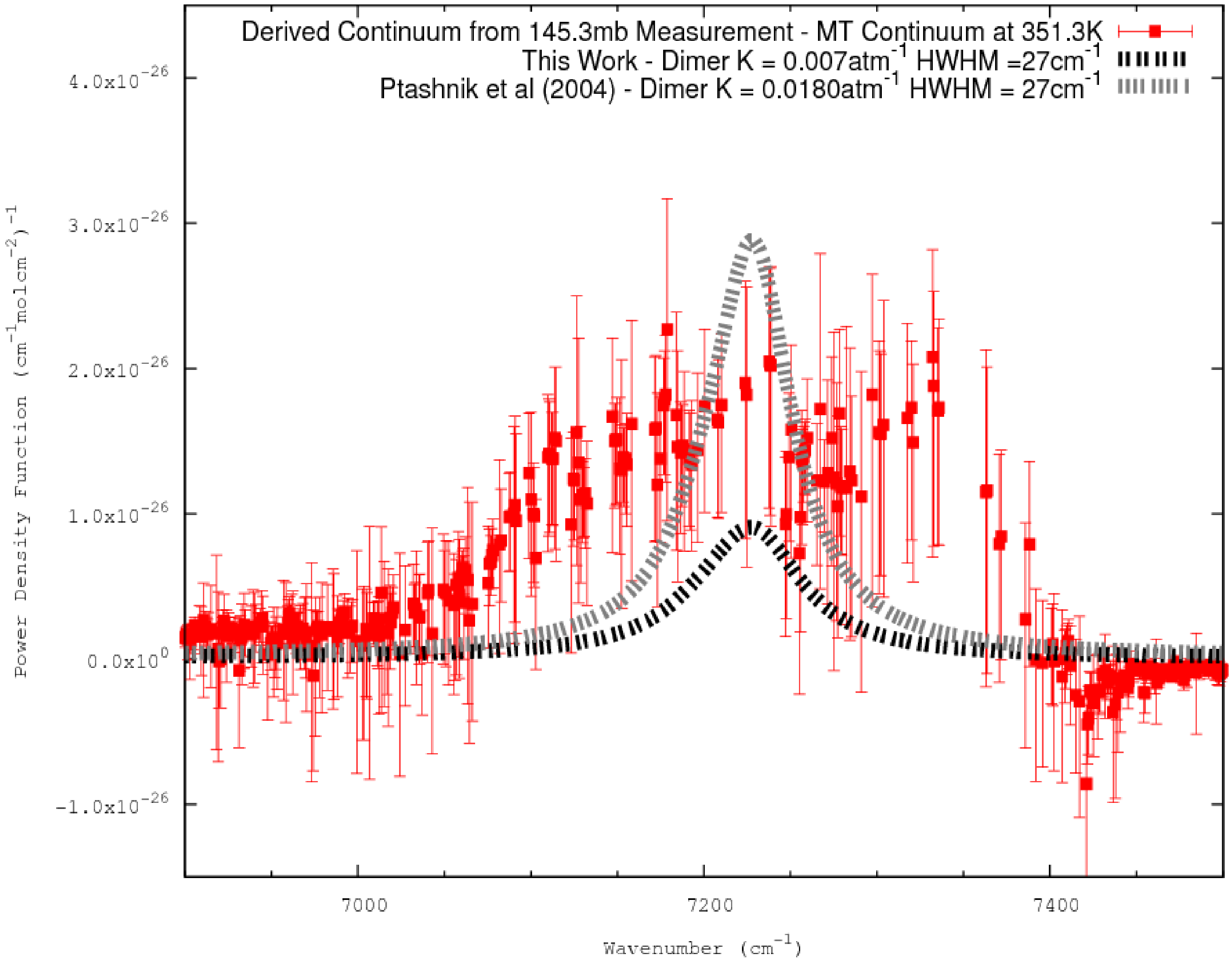
The derived Continuum with M&T Continuum subtracted 5000-5600cm^{-1} (2.0-1.8μm) Compared to Predicted Dimer

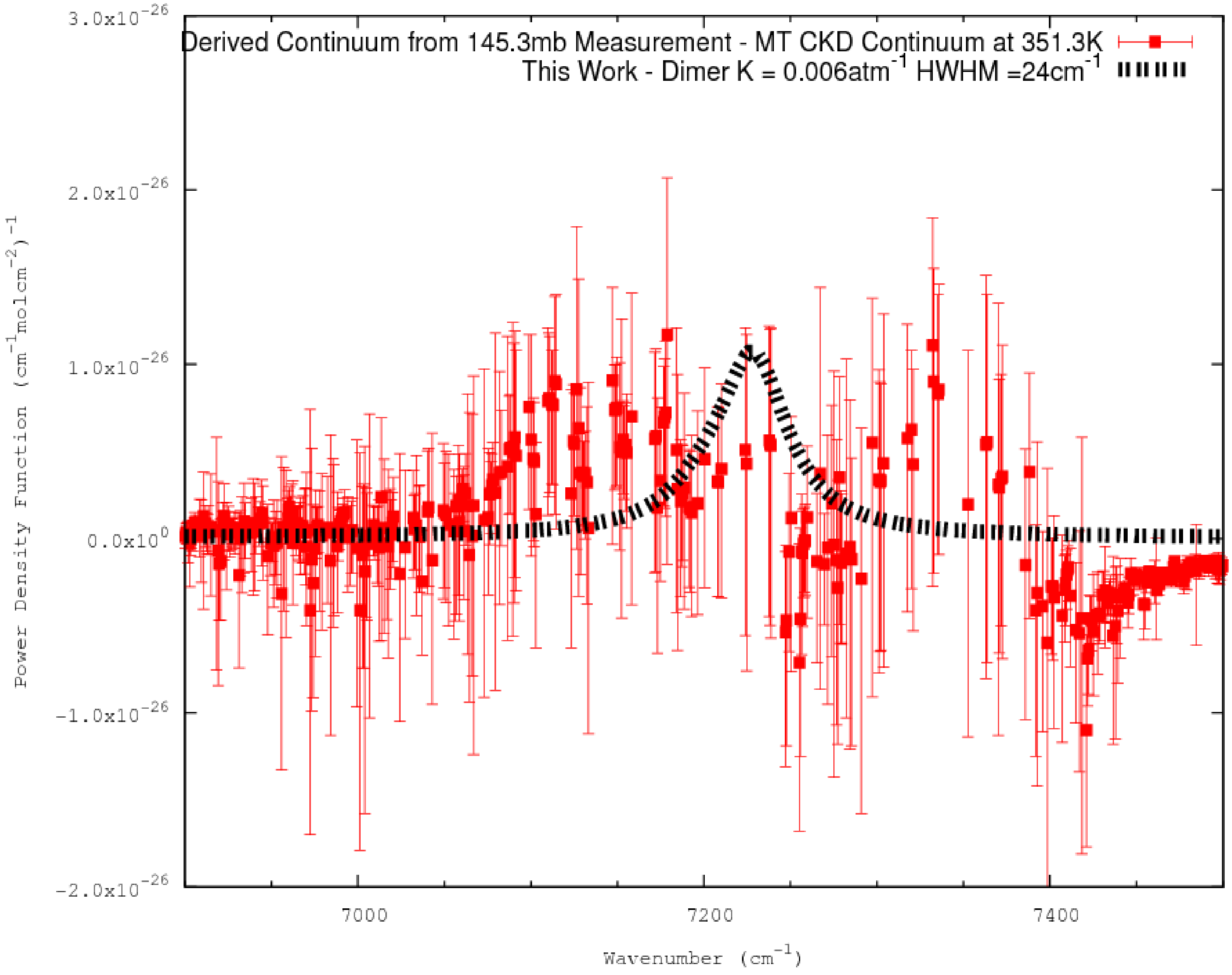


The derived Continuum with MT_CKD Continuum subtracted 5000-5600cm^{-1}(2.0-1.8μm) Compared to that predicted Dimer



Comparing Derived Continuum Theory in 6900-7500cm-1(2.0-1.8μm)





Derived Continuum from 145.3mb Measurement - MT CKD Continuum at 351.3K
This Work - Dimer K = 0.006atm^{-1} HWHM =24cm^{-1}
3.0x10^{-26}
2.0x10^{-26}
1.0x10^{-26}
0.0x10^{0}
-1.0x10^{-26}
-2.0x10^{-26}
Power Density Function (cm^{-1}molcm^{-2})$^{-1}$
7000
7200
7400
Wavenumber (cm^{-1})