The NIR absorption spectrum of water vapor by CRDS between 1.26-1.70 µm: *Complete empirical line list & Continuum absorption*

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Outline

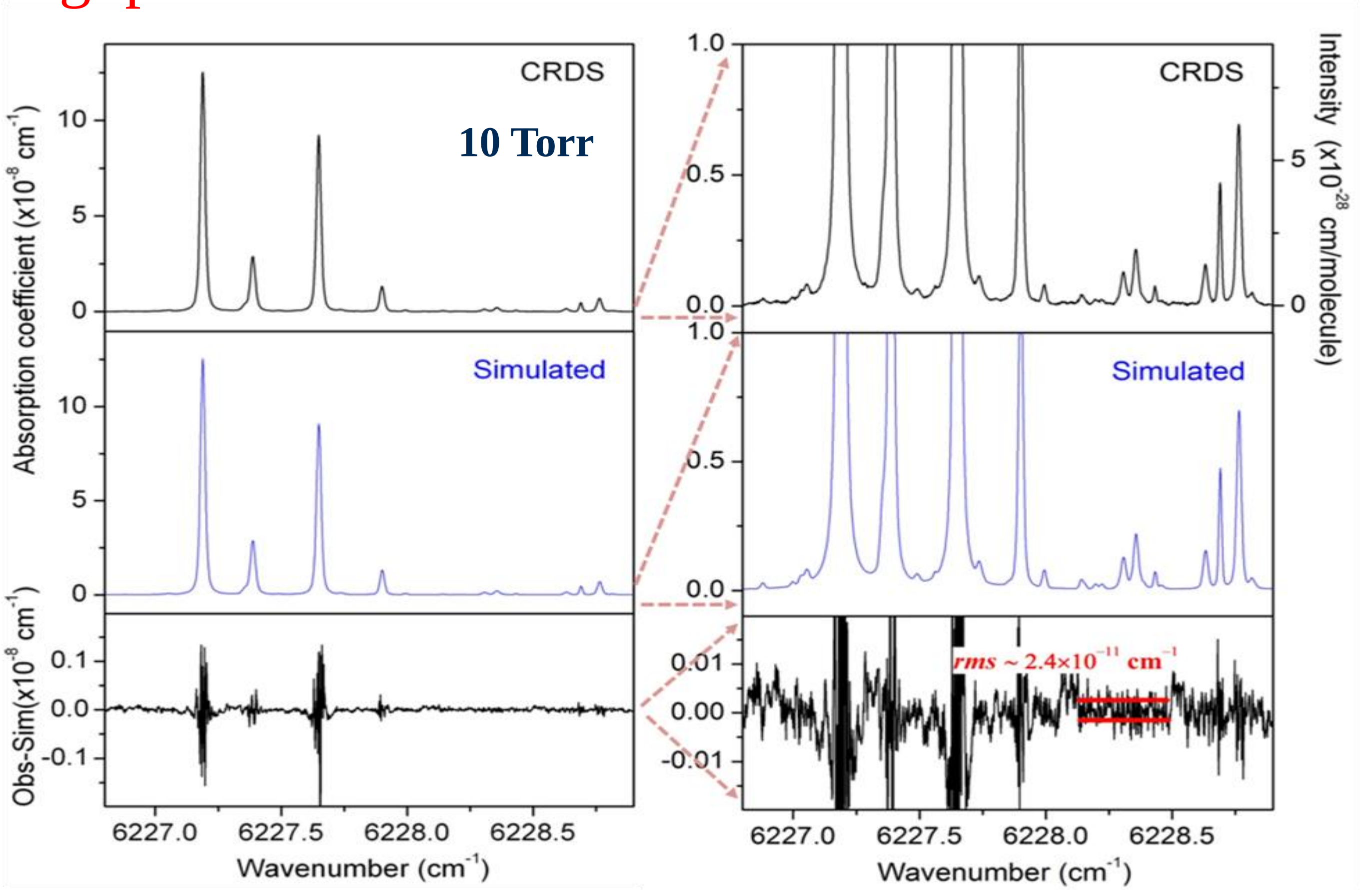
- Line list for water vapor (1.26 -1.70 µm region)
- The self-continuum in the 1.6 µm window
- Conclusions and outlooks

Our CRDS spectrometers

- High sensitivity: α_{min}~5×10^{-11} cm^{-1} (typ. in routine)
- High dynamic range: > 4 orders of magnitude
- Large spectral coverage: 1.20 – 1.70 µm

Fit of the recorded CRDS spectra

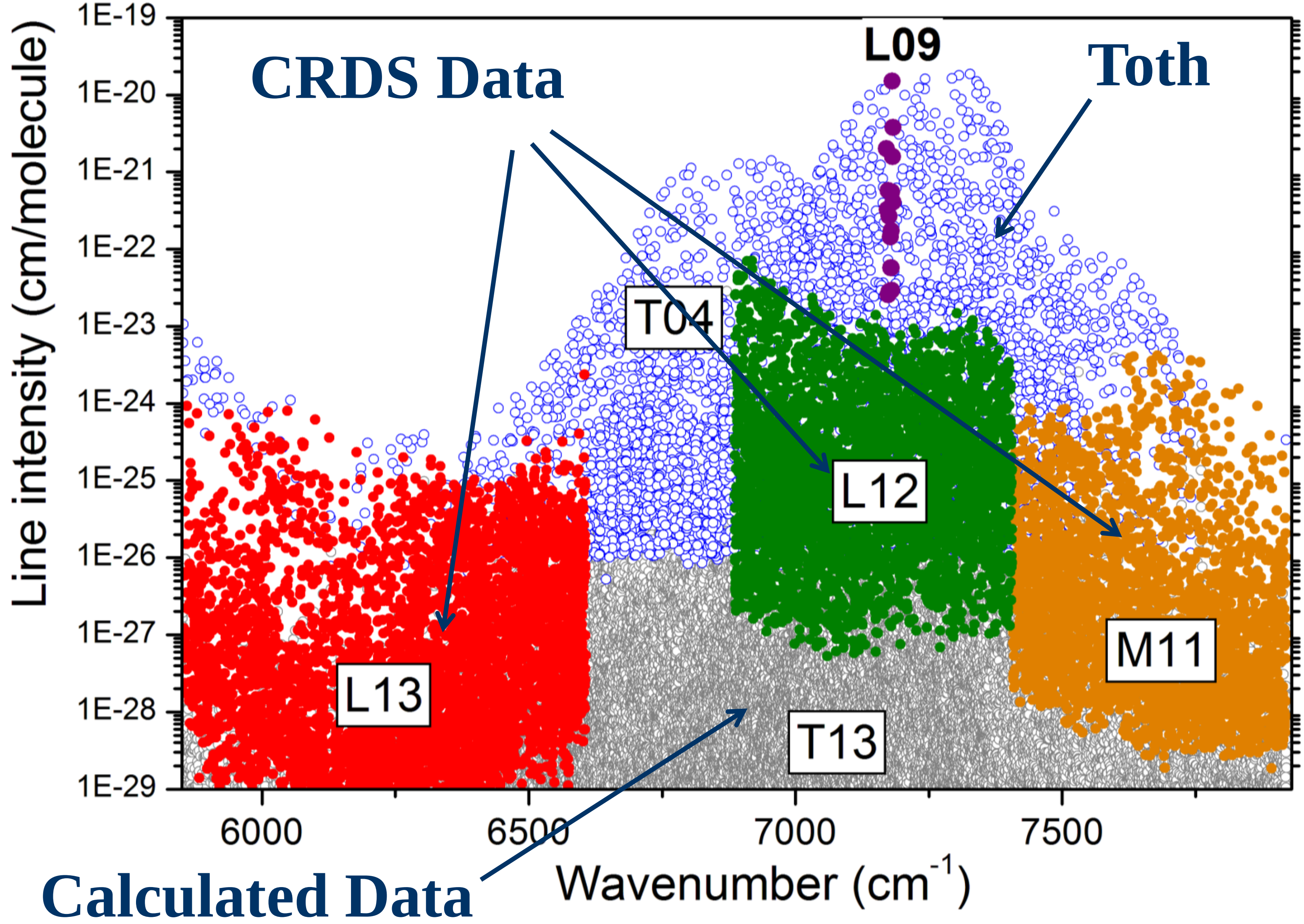
A Voigt profile is used for each observed lines.



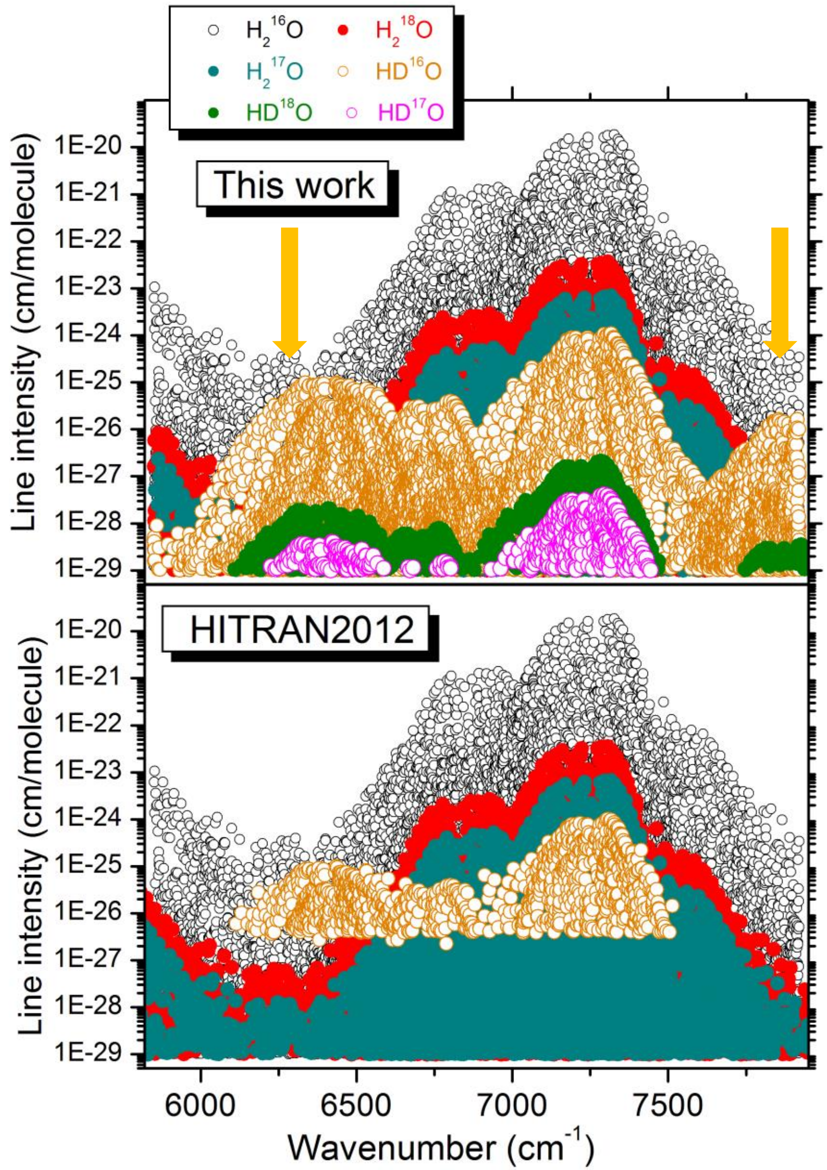
→ List of empirical positions and intensities

Origin of the data in our line list

M11: Mikhailenko *et al*, JMS 2011 L12: Leshchishina *et al*, JQSRT 2012
L13: Leshchishina *et al*, JQSRT 2013



Overview comparison with HITRAN2012



This work: 38 138 lines (for the four main isotopologues)

+1372 $HD^{18}O$ lines

+ 600 $HD^{17}O$ lines

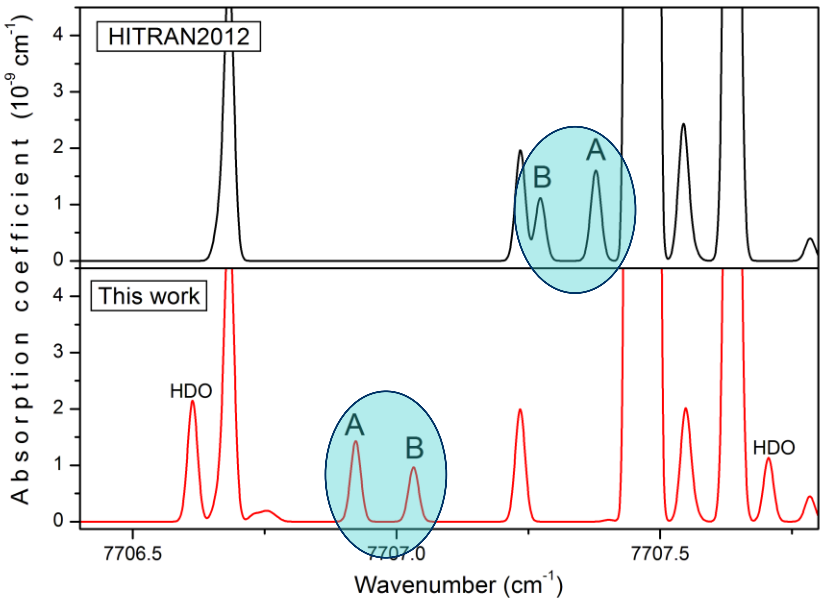
HITRAN: 31 381 lines

Difference mainly due to $HD^{16}O$

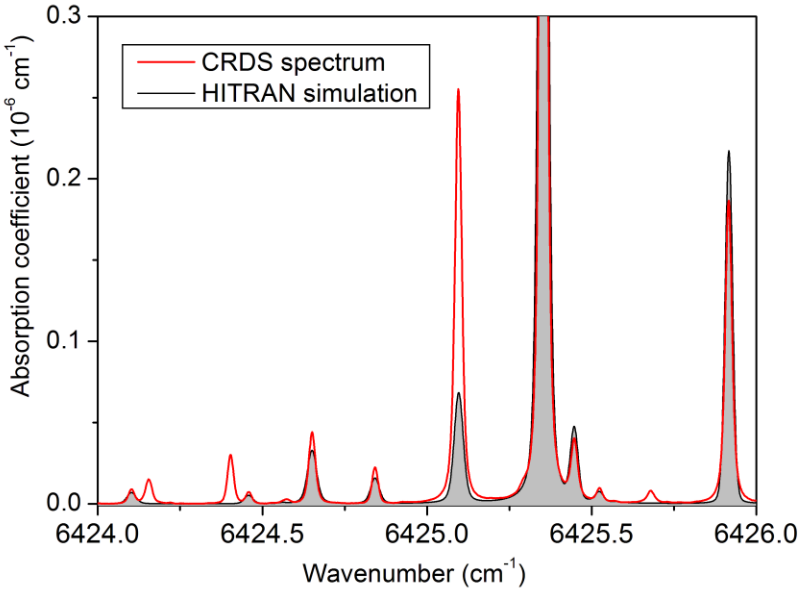
→ Important limitation in the transparency windows

Some deficiencies in HITRAN2012

On positions…



…and intensities



Summary

- Complete: *ν*, *S*, *E''* , unique assig. for 40 290 transitions for the 6 major isotopologues.
- Empirical: positions rely on exp. determined energy levels.
- Evidence of some deficiencies in HITRAN2012: lack of HDO lines + some inaccurate pos. and intensities.

Adopted for the next edition of the GEISA database

Improvements on line position accuracy

Typ. accuracy: 30 MHz (1×10^{-3} cm^{-1}) obtained with wavemeters

With a frequency comb (On fly measurements of $\nu_{beat\ note}$ between DFB and comb teeth)

Accuracy:

< 500 kHz (without aver.)

~10 kHz (with aver.)

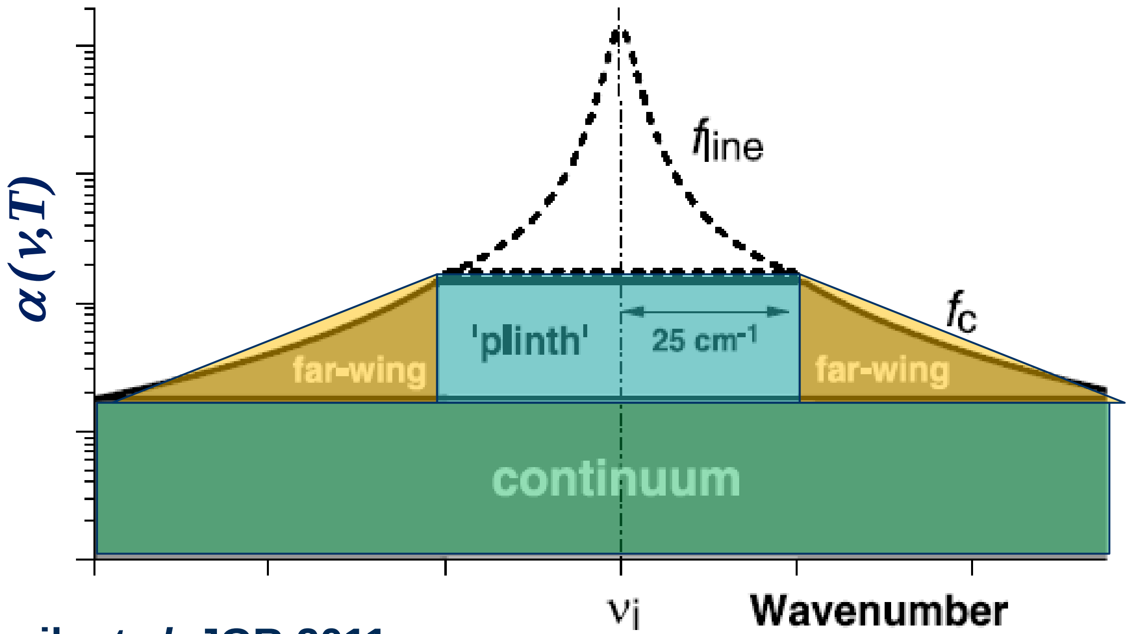
In collab. with Politecnico di Milano

The water vapor self-continuum in the 1.6 μm window

The (arbitrary) definition of the continuum

Continuum = $\alpha_{Meas} - \alpha_{WML}$

α_{WML} corresponds to a (Lorentz) profile within 25 cm^{-1} of **monomer** line centre, without the 25 cm^{-1} ('plinth').

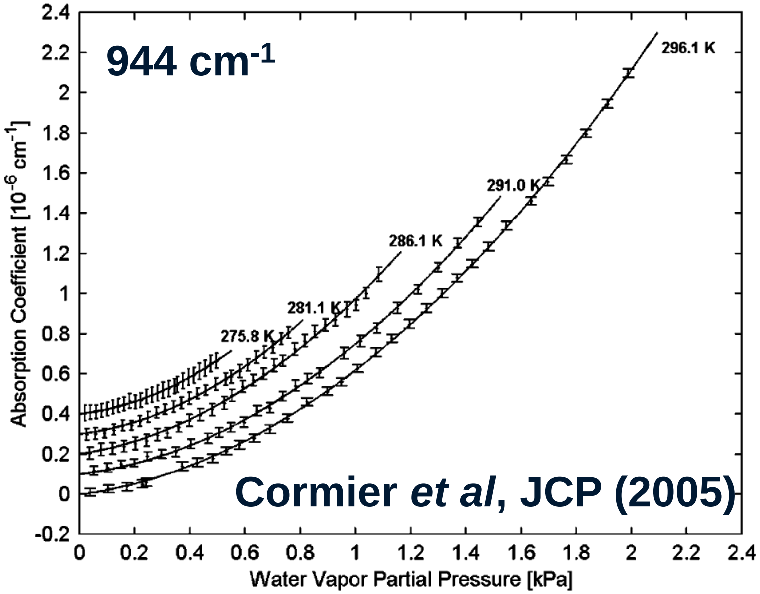


Ptashnik *et al*, JGR 2011

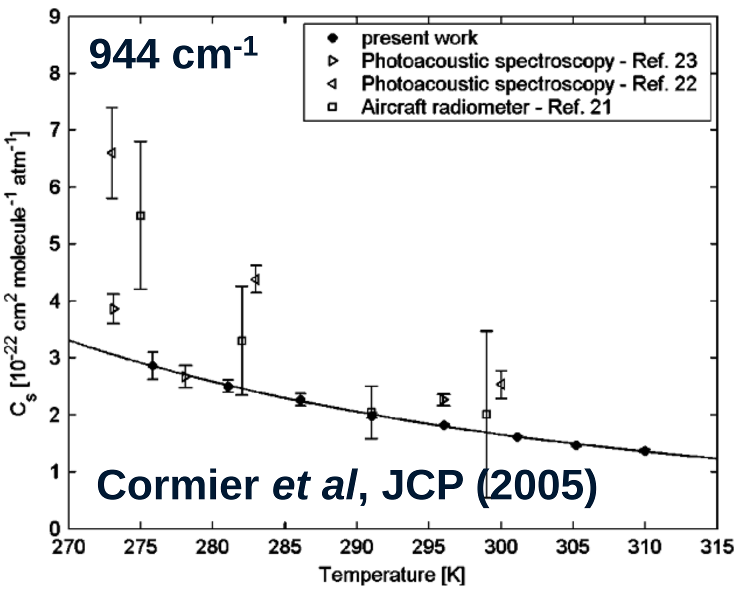
Characteristics of the continuum

$$\alpha_{WC}(\nu, T) = C_s(\nu, T) P^2 / kT$$

Cross-section
(cm² molec⁻¹ atm⁻¹)



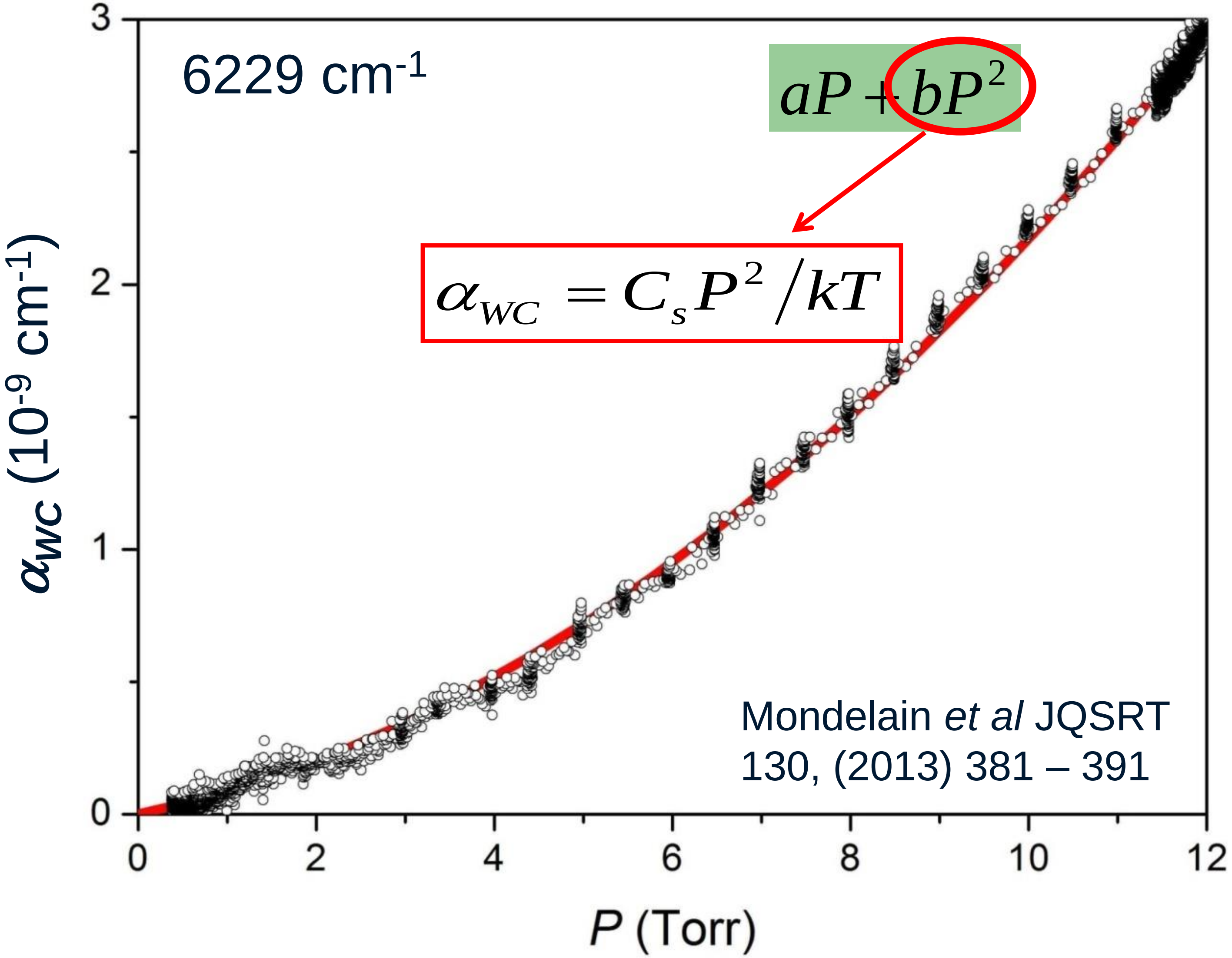
+ Negative temp dep



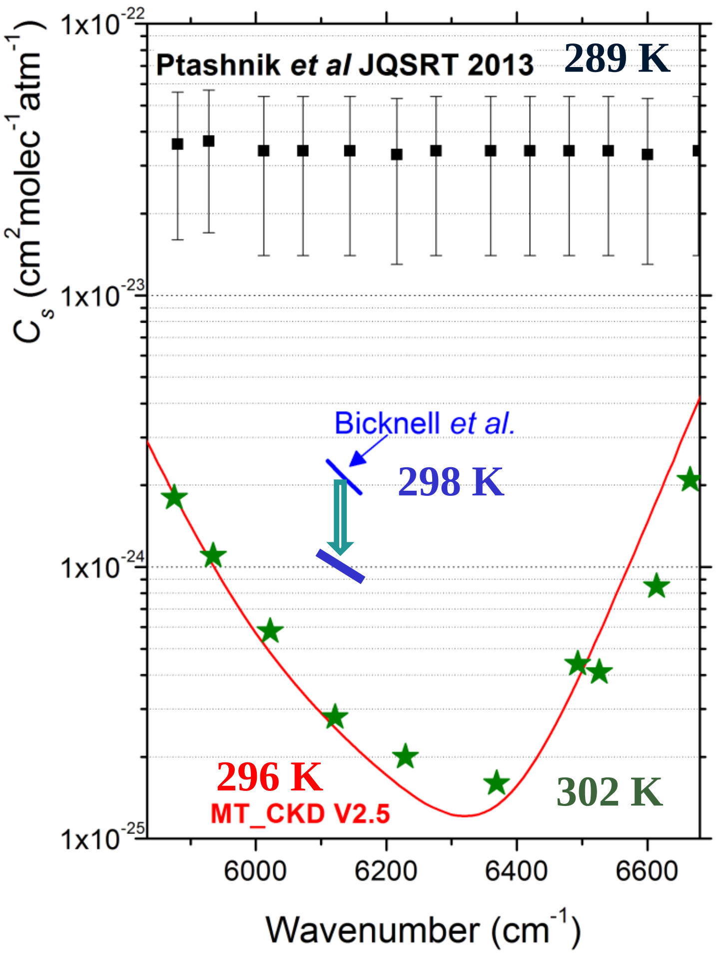
Two components (in the atmosphere):
- self-continuum
- foreign-continuum

Retrieval of the self-continuum

$$\alpha(\nu) = \alpha_{WML} + \alpha_{WC}$$



Comparison with previous experimental results near RT



Ptashnik *et al*
FTIR spectra from IAO TOMSK (L=612 m)
C_s = (3.4±2)×10^{-23} cm^2 molec^{-1} atm^{-1}

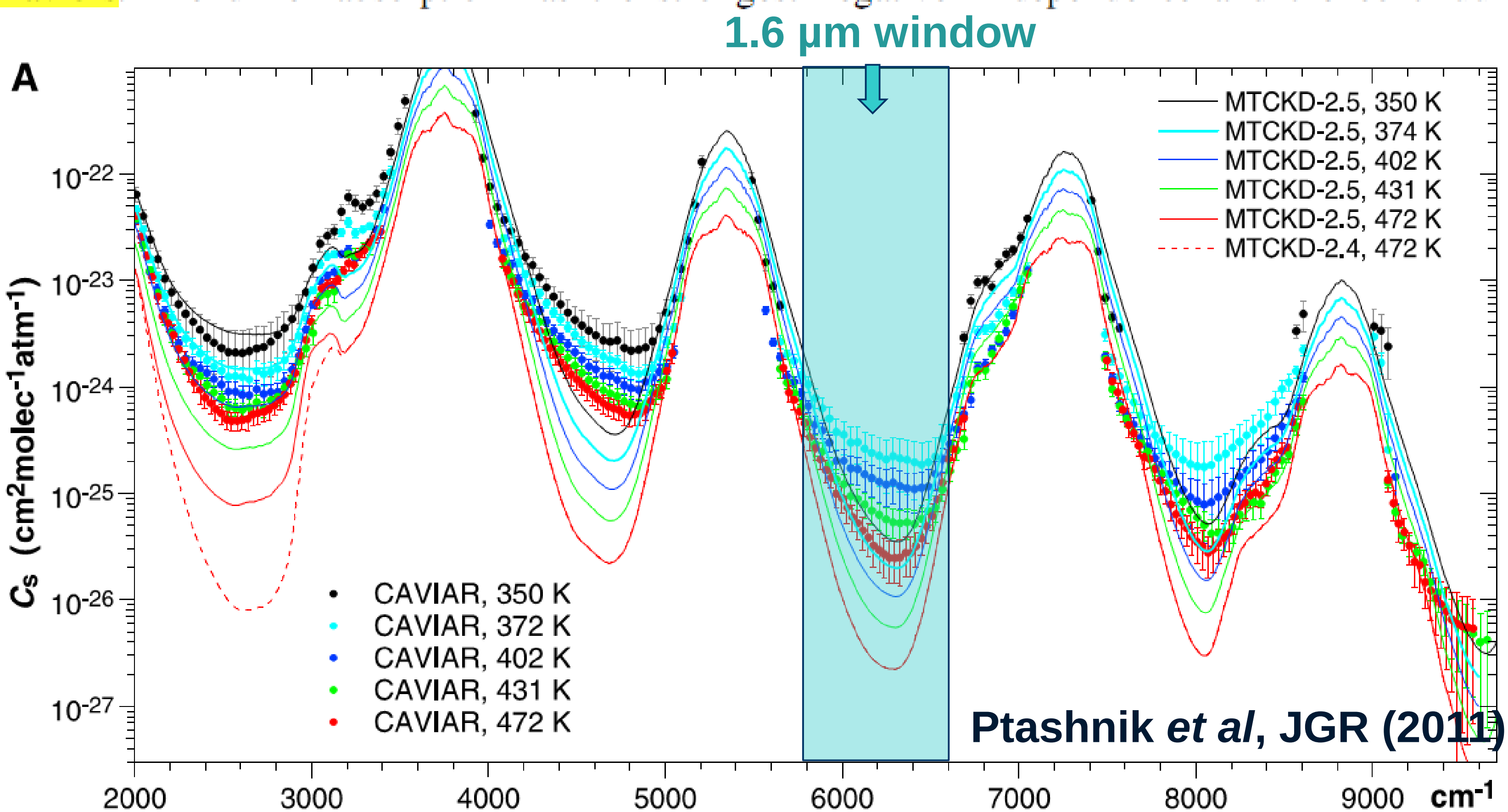
Bicknell *et al*
Calorimetric-interferometric method
Search for low - absorption regions in the 1.6 - and 2.1 -µm atmospheric windows.
J. Dir. Energy 2006;2:151-61.

MT_CKD: semiempirical formulation of the continuum.

Temperature dependence of C_s

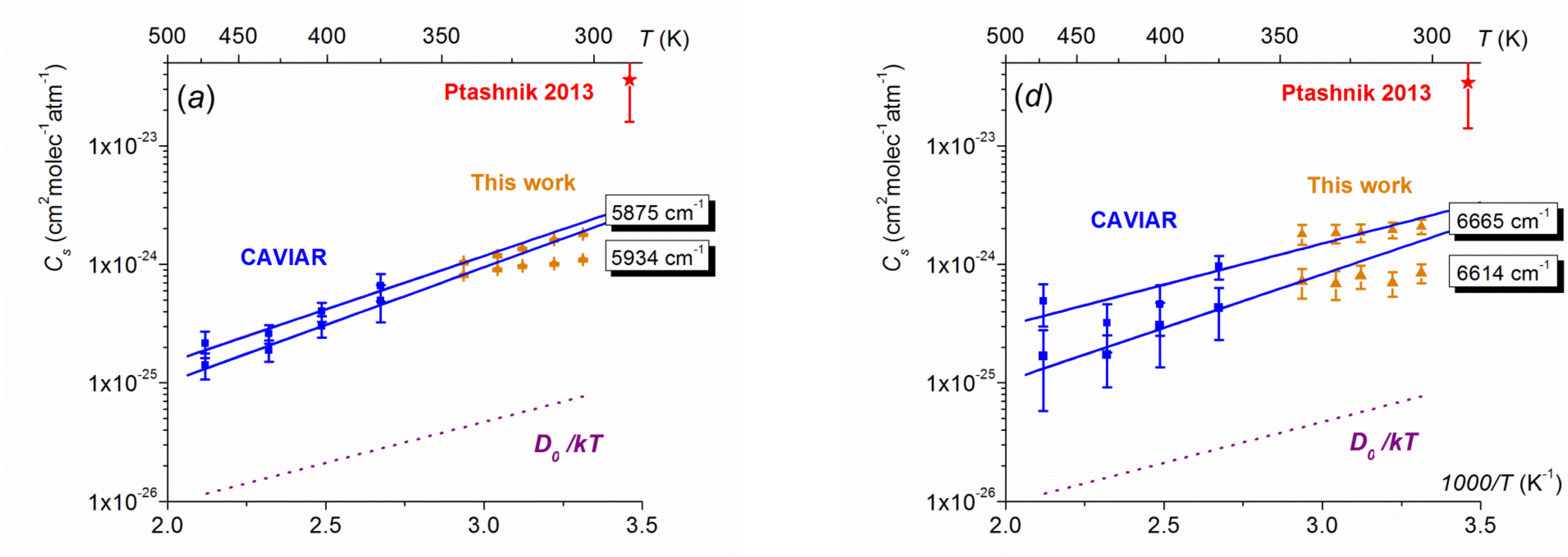
Leforestier *et al*, JCP (2010)

We investigated the magnitude and temperature dependence (T dependence) of the dimer absorption in the region of 0–600 cm^{-1} and the collision-induced absorption (CIA) in the region of 0–1150 cm^{-1}. Together with our previous study of the self water-vapor continuum contributions resulting from far-wing line shapes of the allowed H_2O lines in the infrared window between 800 and 1150 cm^{-1}, we find that the three mechanisms have completely different T dependence behaviors. The dimer absorption has the strongest negative T dependence and the continuum

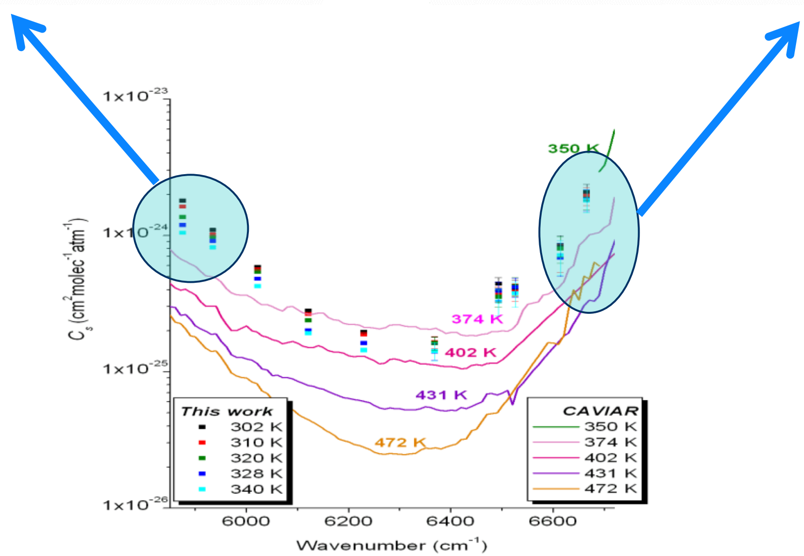


Ptashnik *et al*, JGR (2011)

Comparison with CAVIAR FTS measurements



Mondelain *et al*, JGR (2014)



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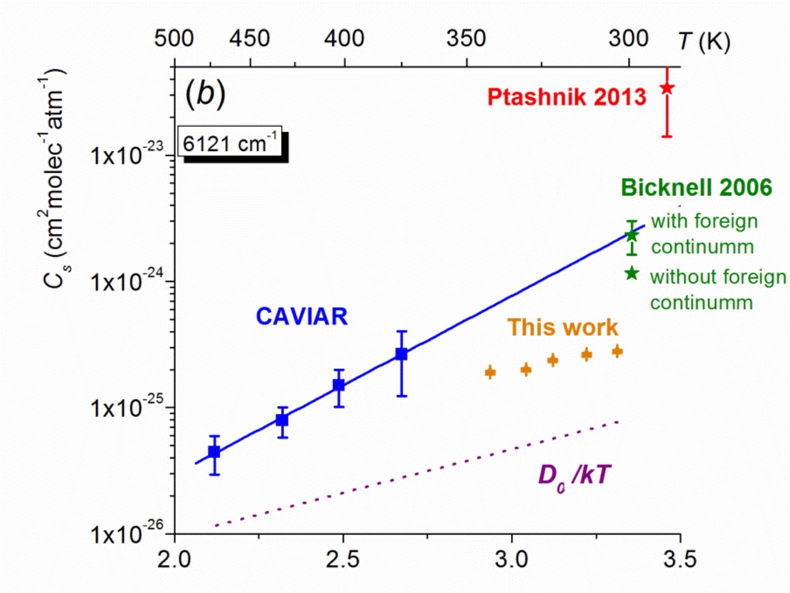
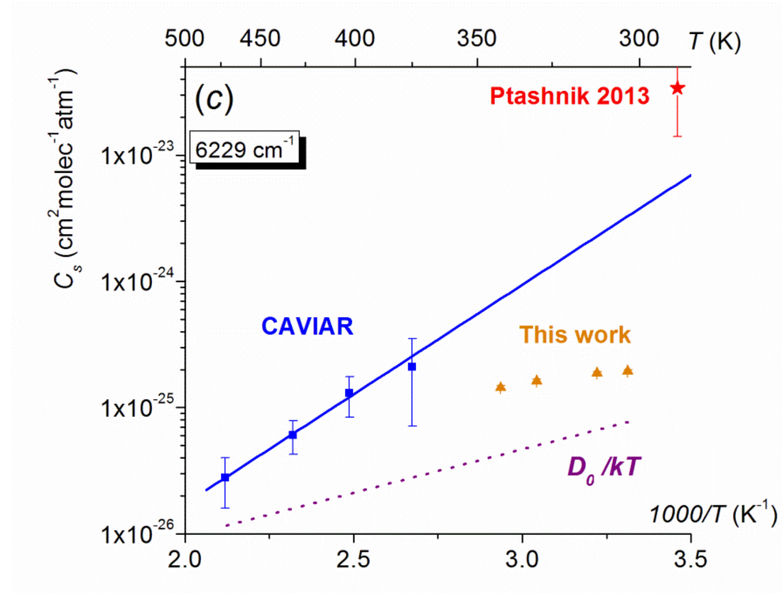
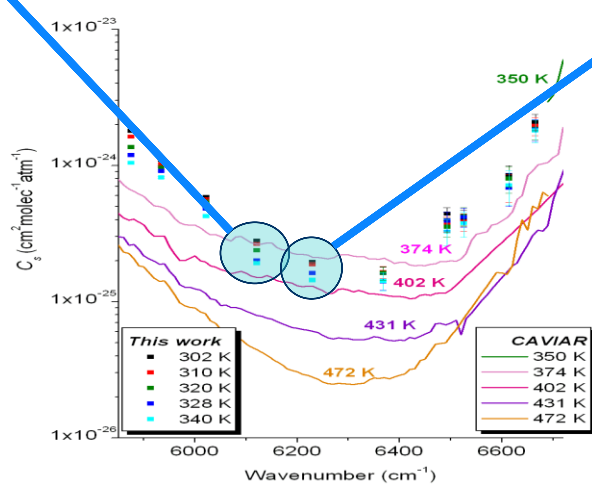
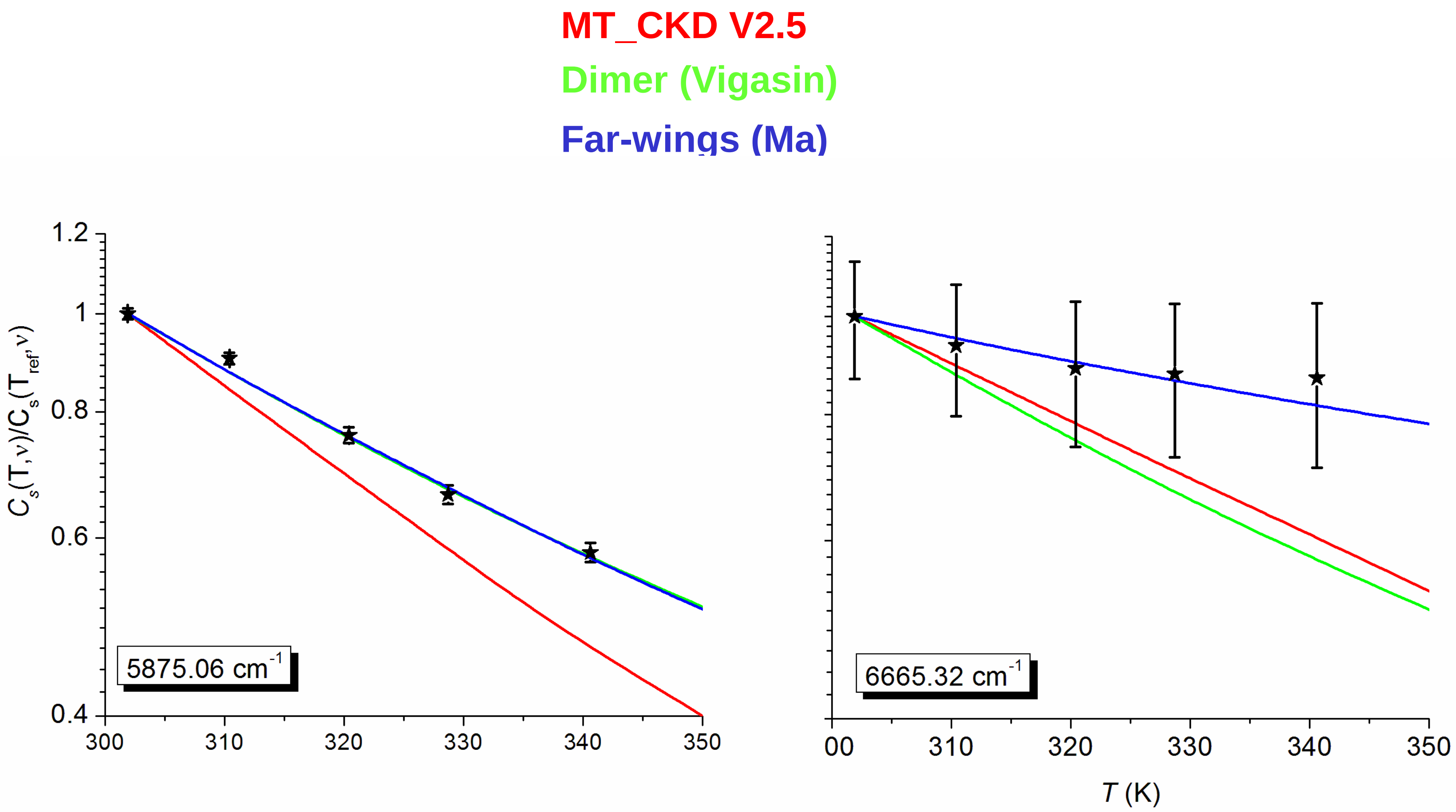




Mondelain *et al*, JGR (2014)

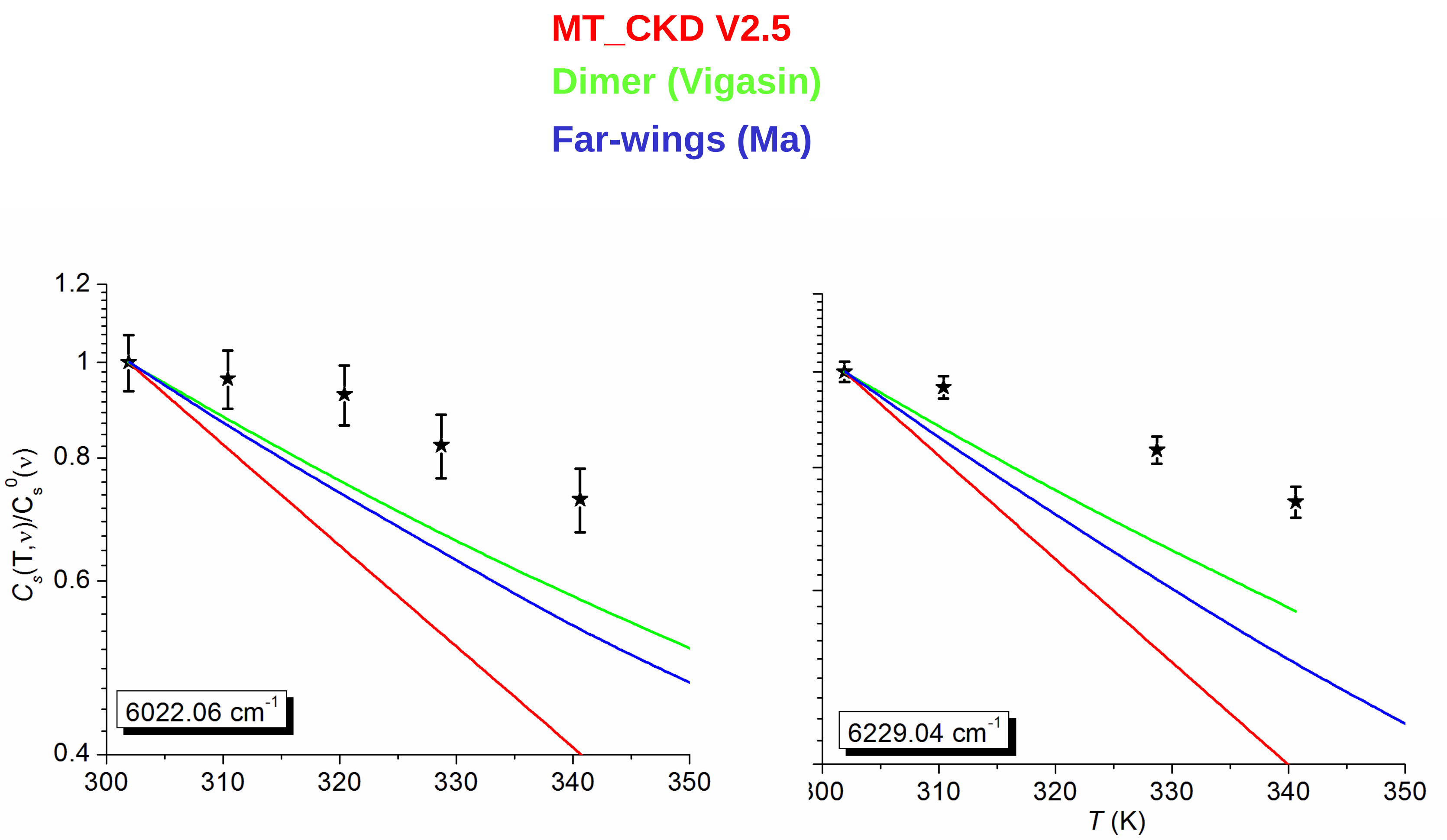


Comparison with models (At the edges)



Mondelain *et al*, JGR (2014)

Comparison with models (At the center)



Mondelain *et al*, JGR (2014)

Conclusion & Perspectives

- Our results provide constraints for absolute cross-sections and their temp. dependence.
- CRDS is a good alternative to FTS to measure water continuum in the transparency windows

(real time monitoring at fixed spectral points during P ramp)

Perspectives:

- Clarify the contribution of adsorbed water with CRDS cells with different lengths
- Extend the T range
- Other TW (2.3 and 1.25 µm)
- Foreign continuum

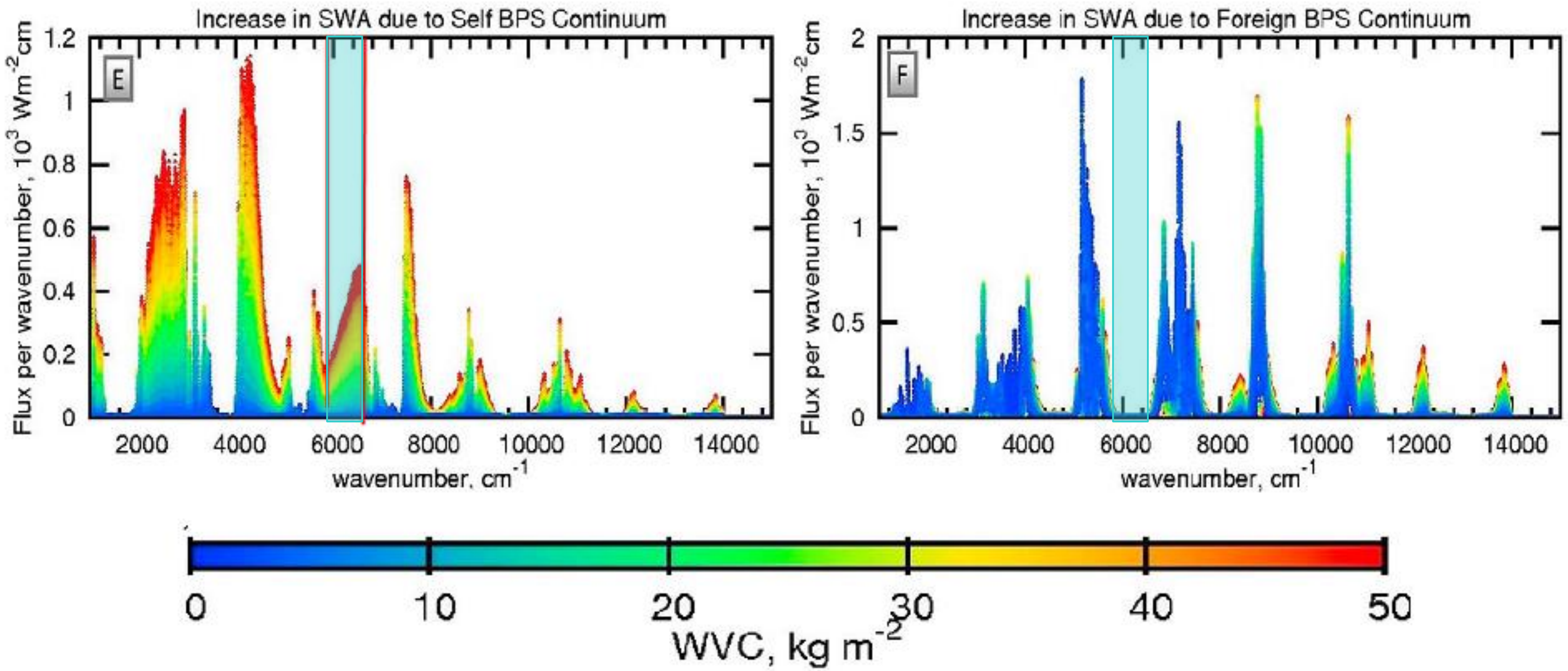
Many thanks to…

A. Campargue, S. Kassi, S. Mikhailenko, S. Manigand, A. Aradj

Q. Ma and A. Vigasin

And the LEFE-ChAt program
And LIA SAMIA

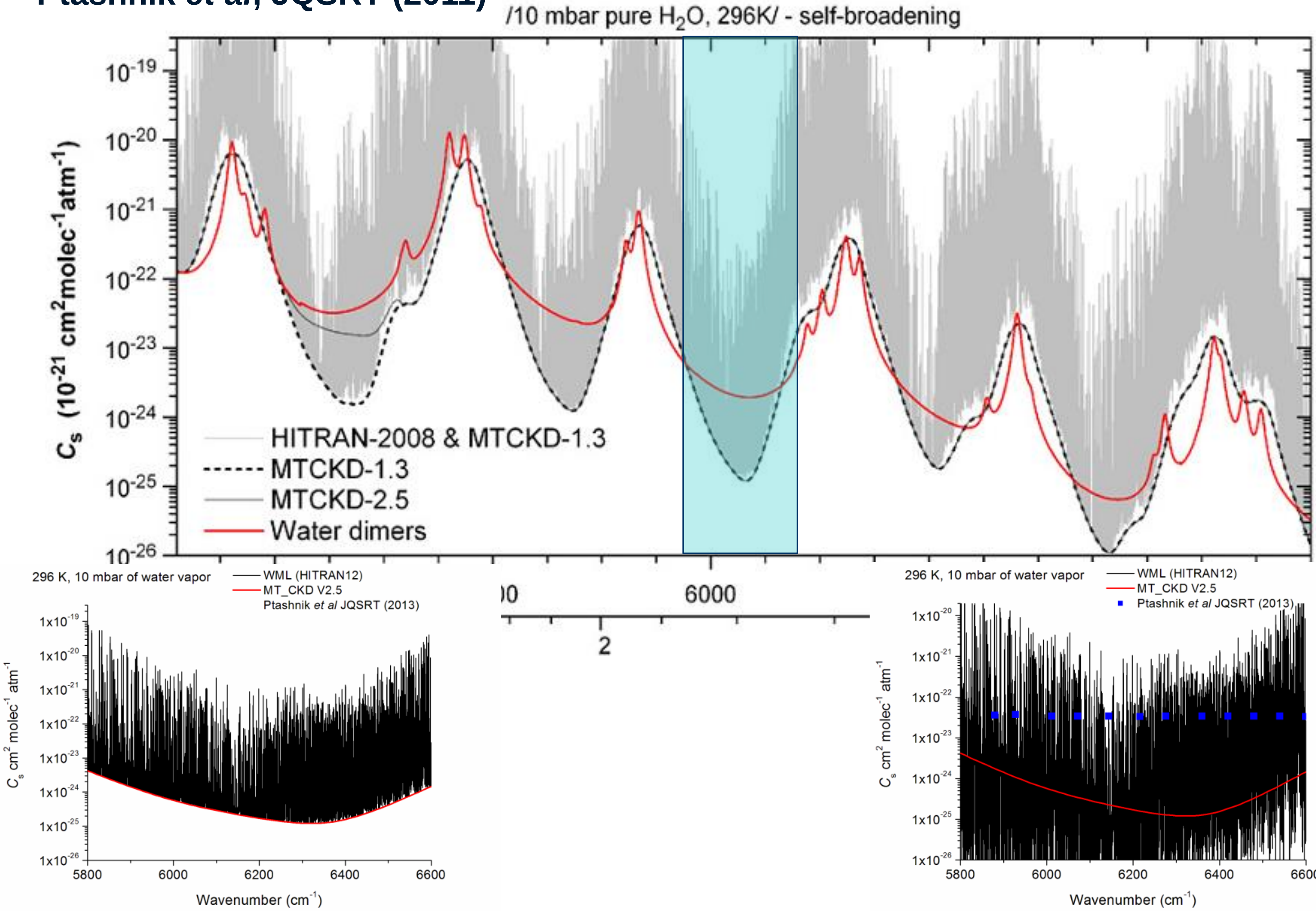
Increase of the absorption in SWA region due to BPS continuum



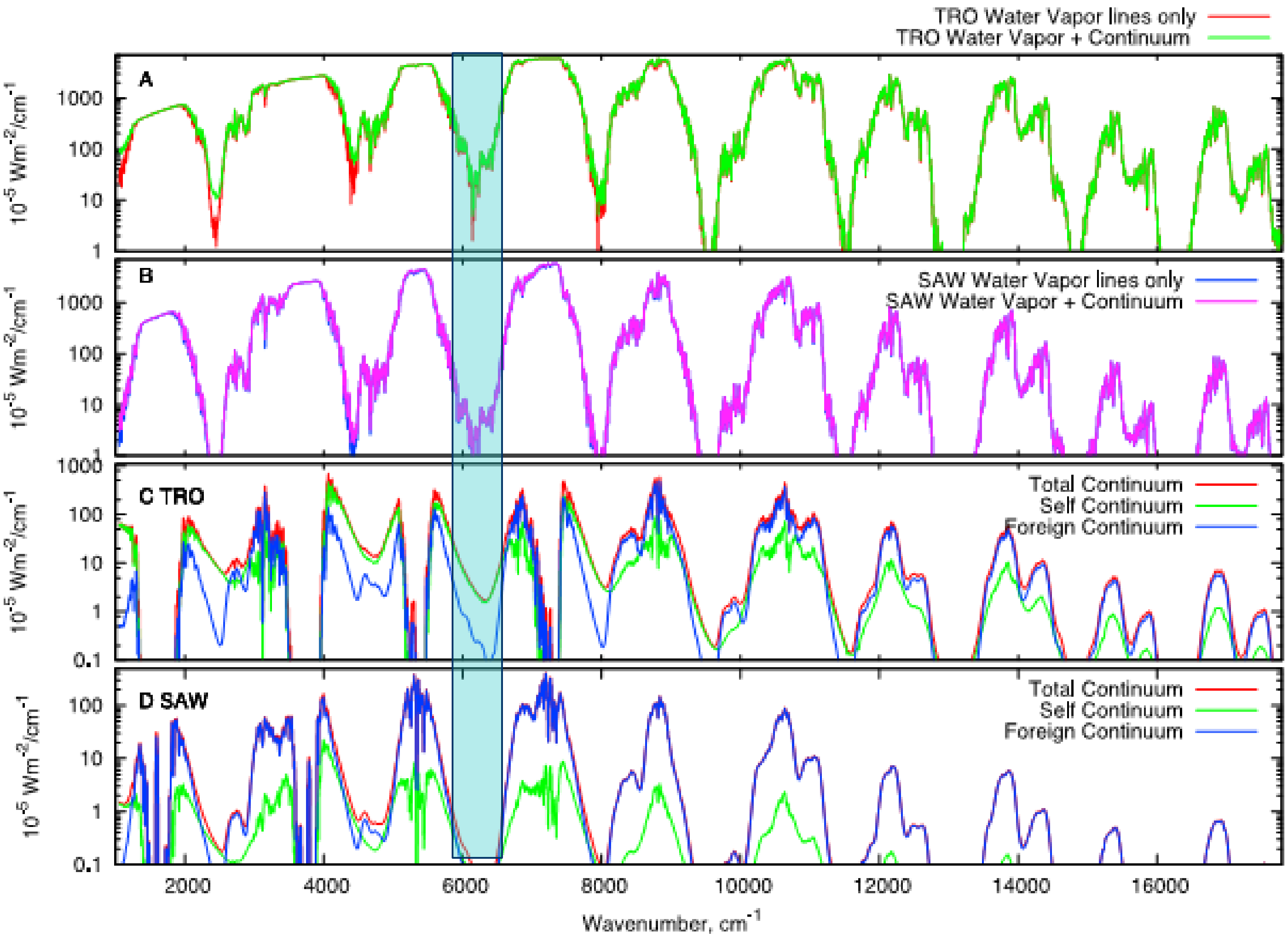
Paynter and Ramaswamy, JGR (2012)

Absorption cross-section due to WML and continuum

Ptashnik *et al*, JQSRT (2011)

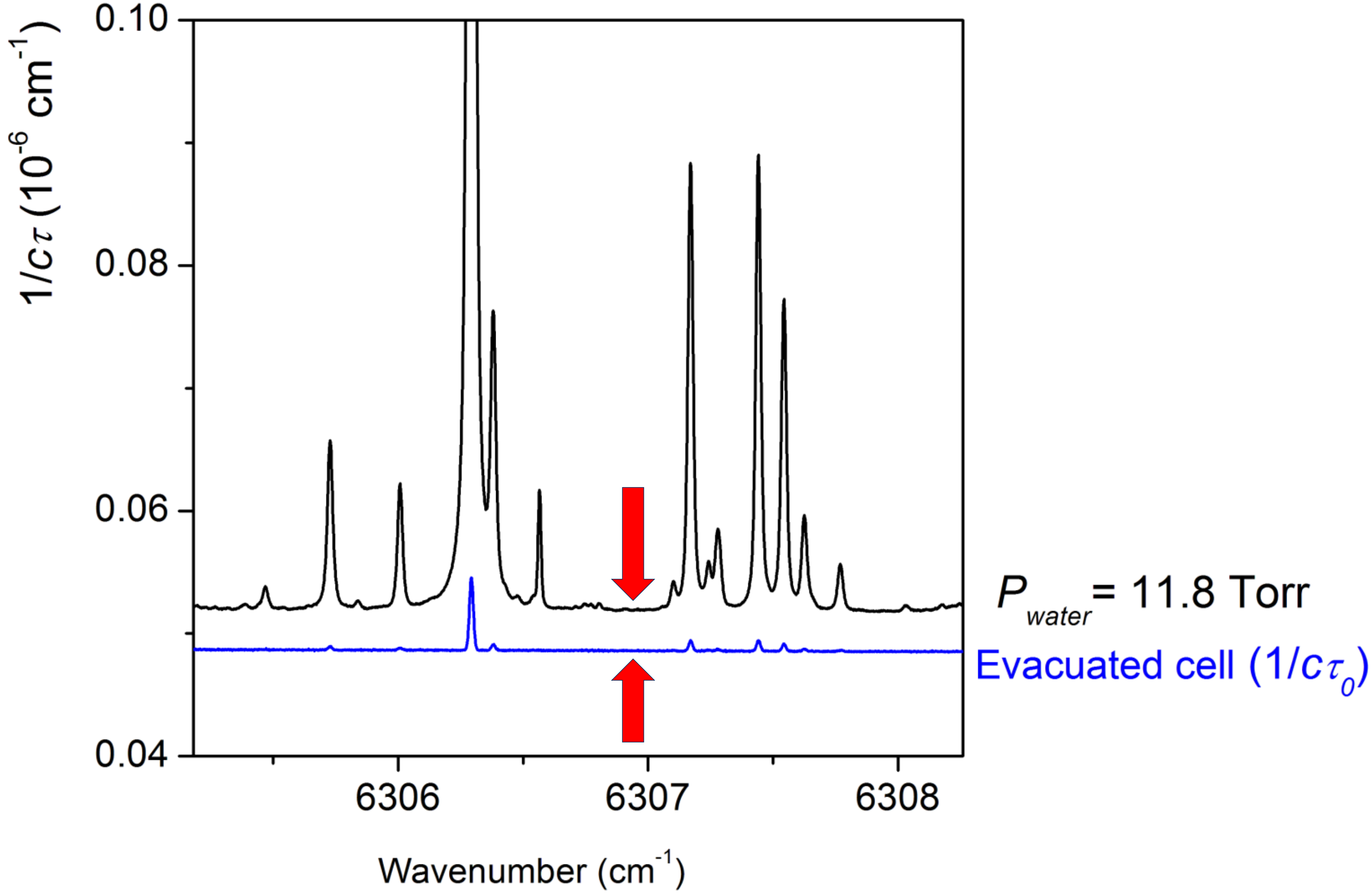


Increase of the absorption in SWA region due to MT_CKD V2.5 continuum

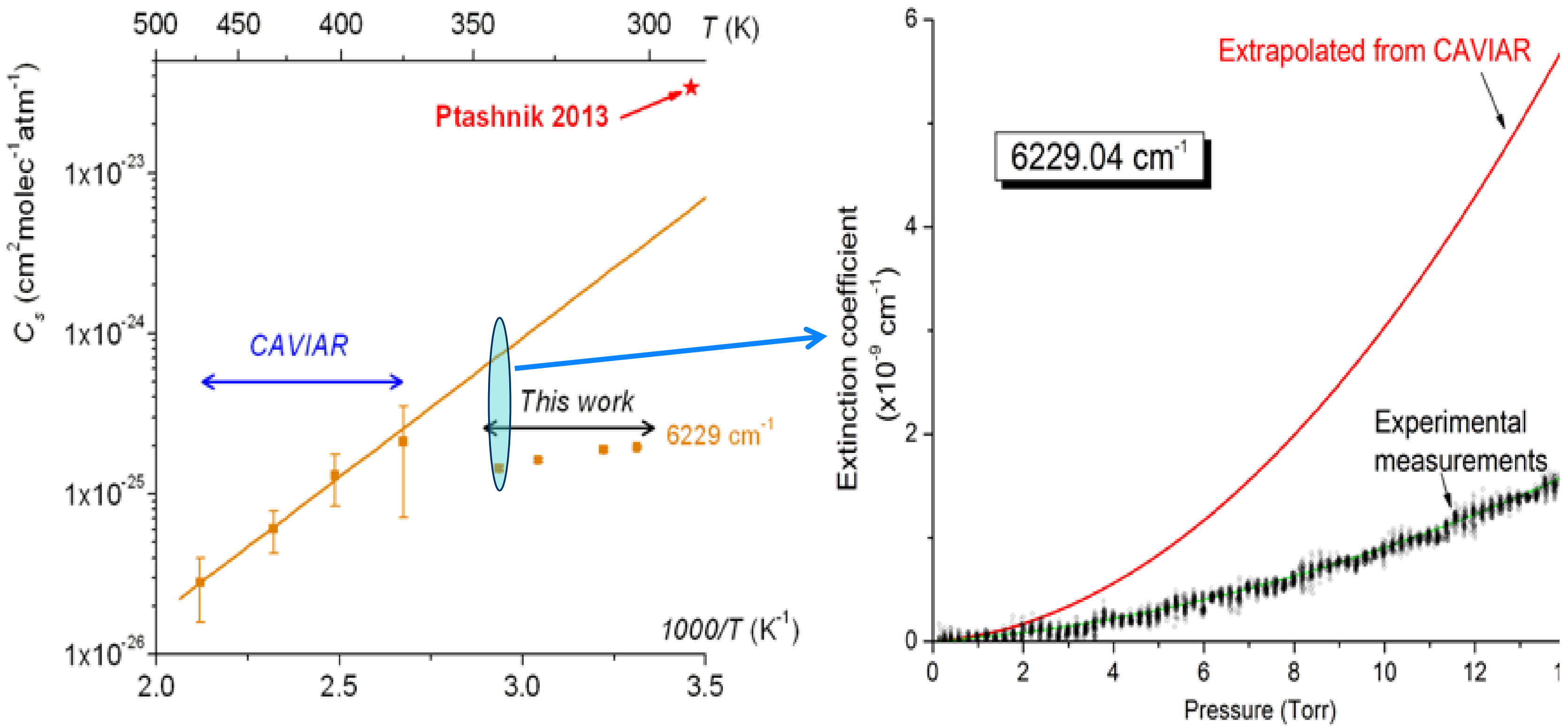


Paynter and Ramaswamy, JGR (2011)

The (arbitrary) definition of the continuum



Disagreement with the CAVIAR data
(In the center of the window)



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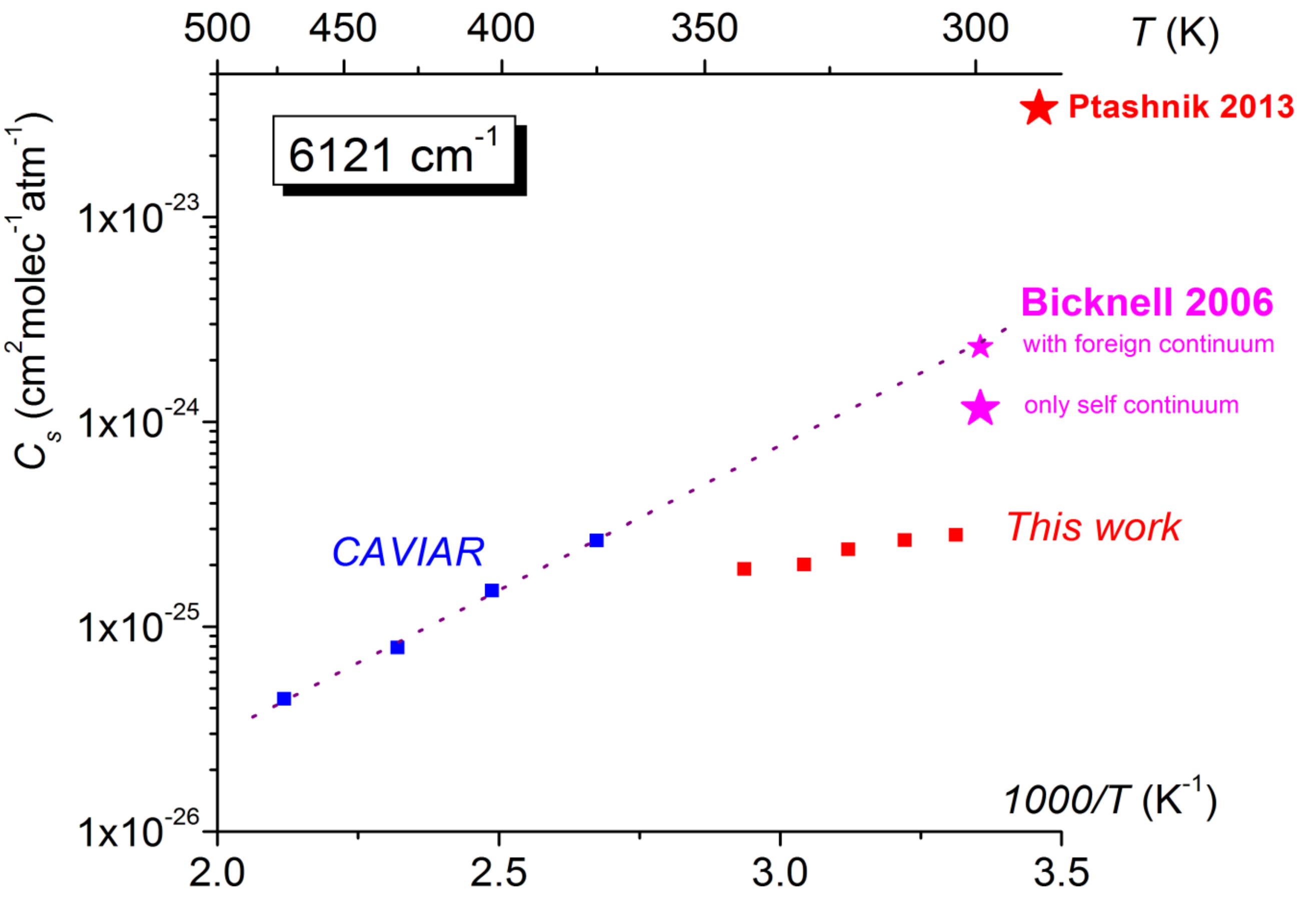
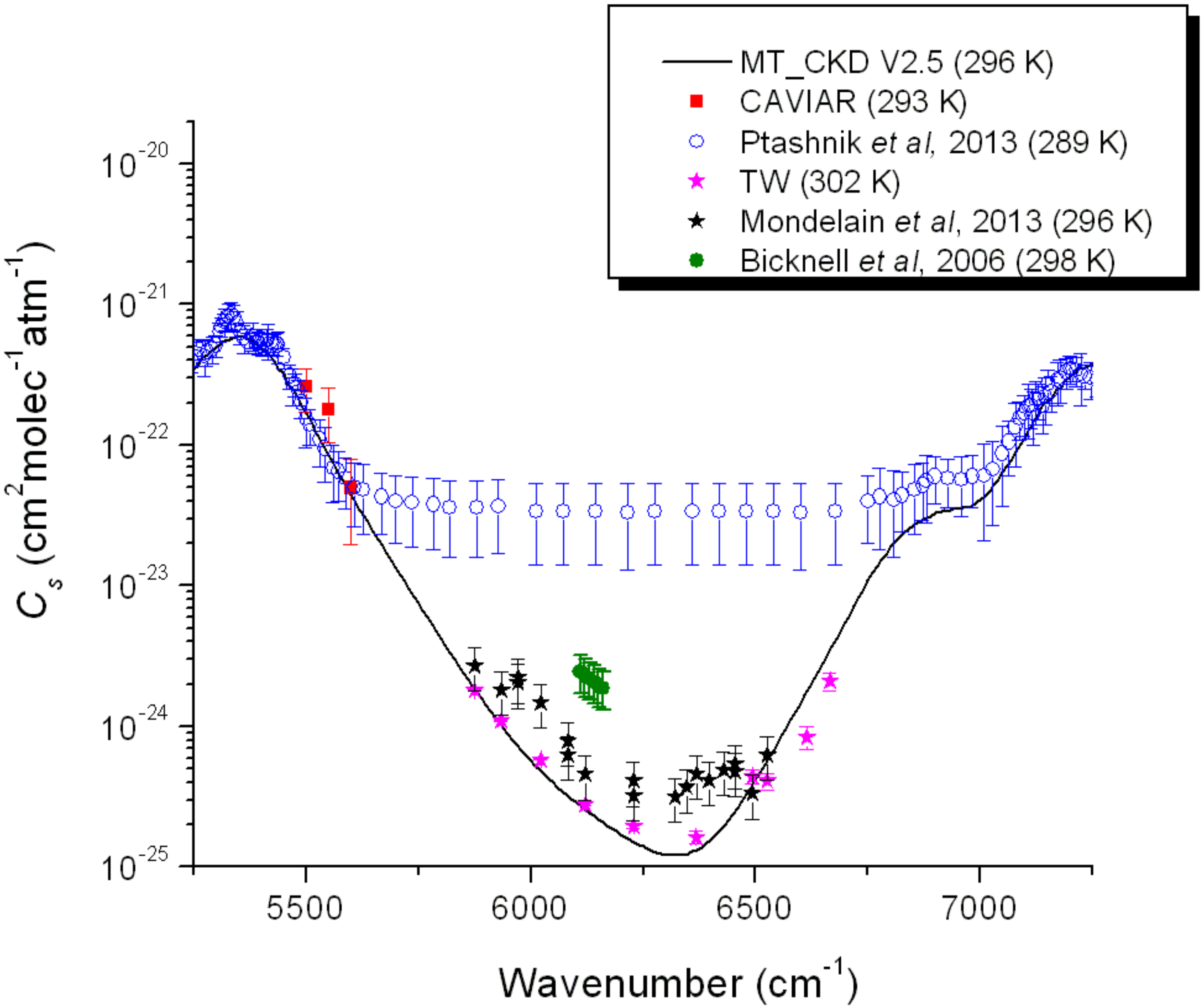


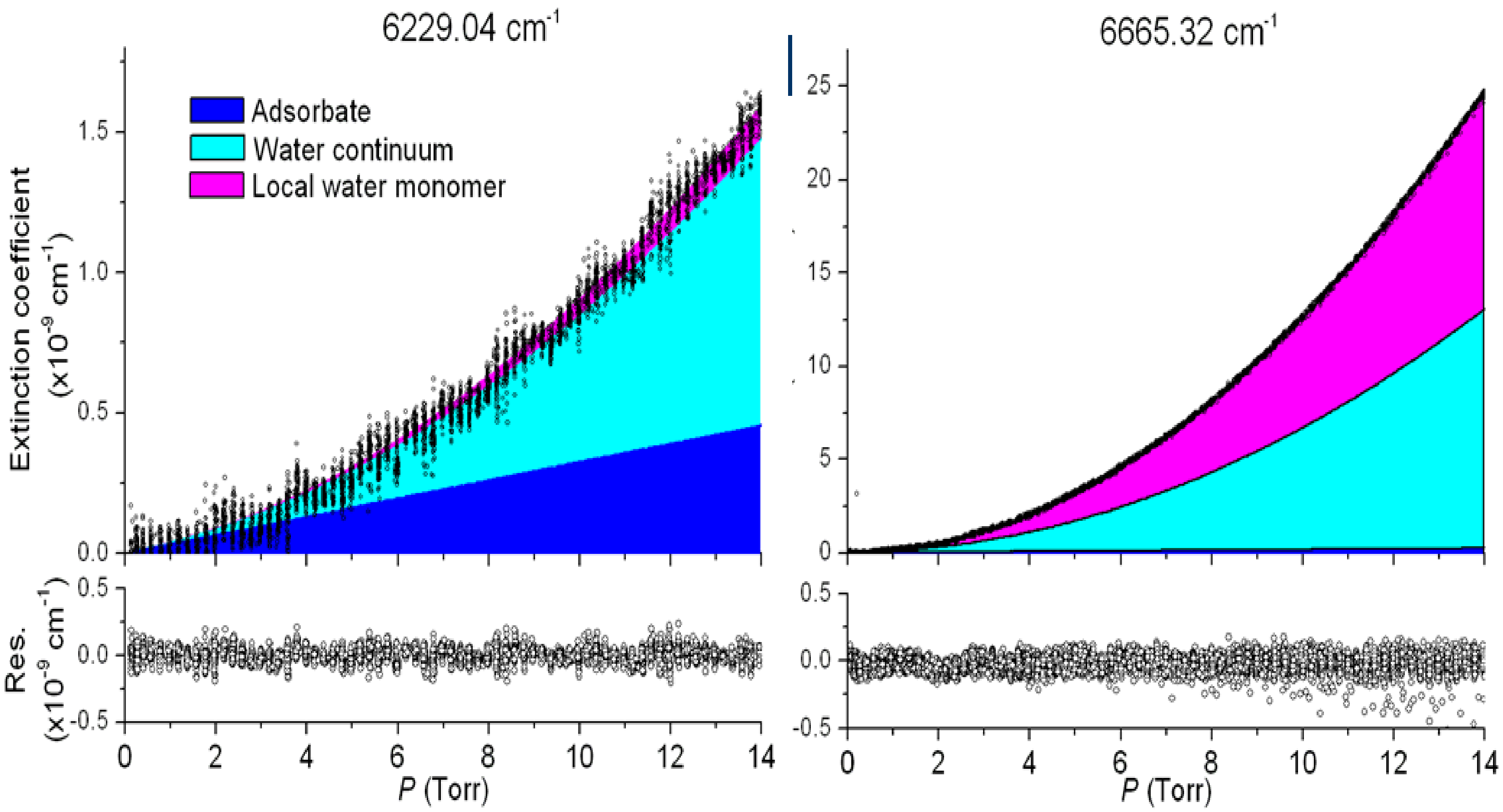
Experimental data at RT In the 1.6 µm window



The different contributions to the extinction coefficient

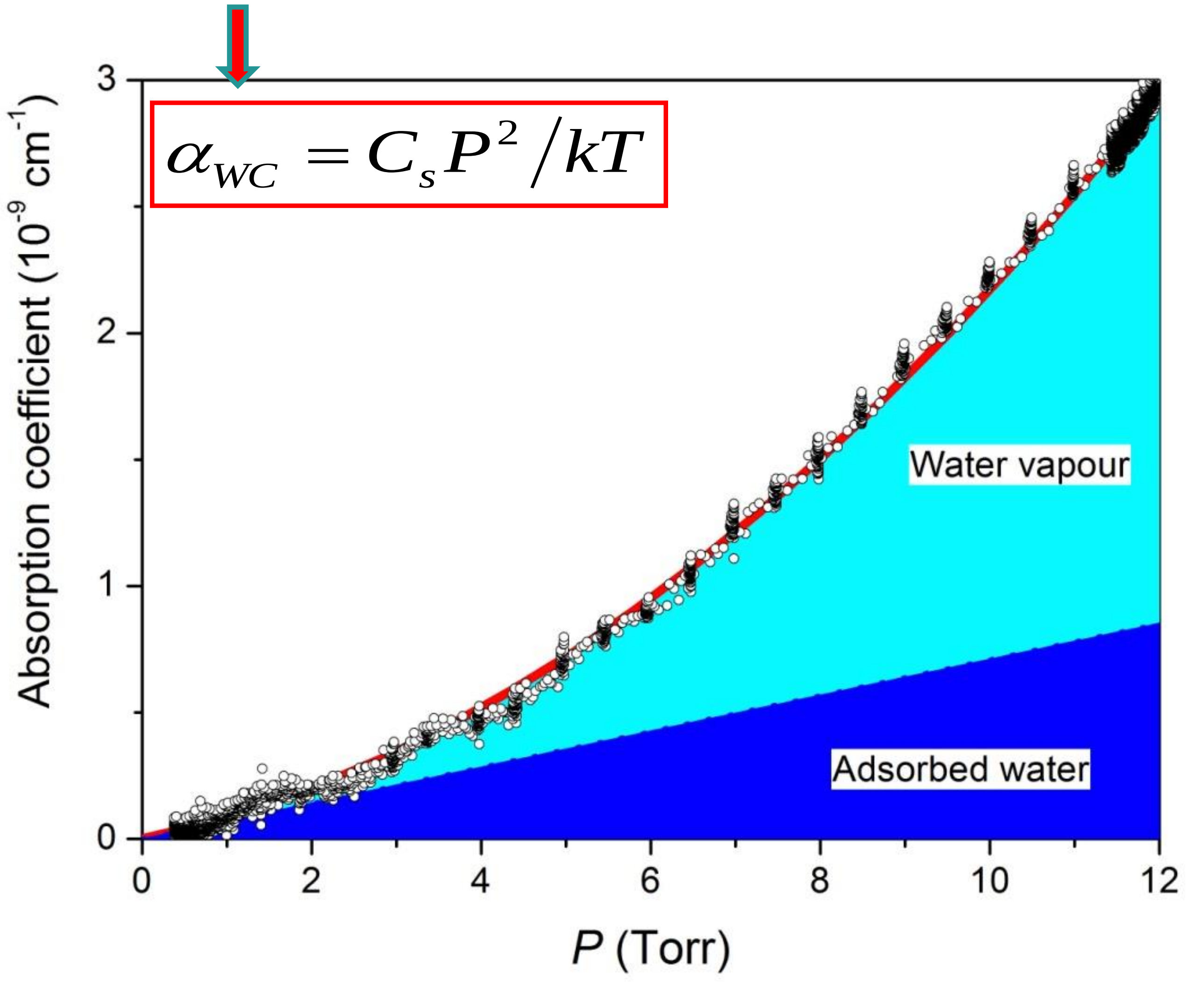
In the center

High energy edge

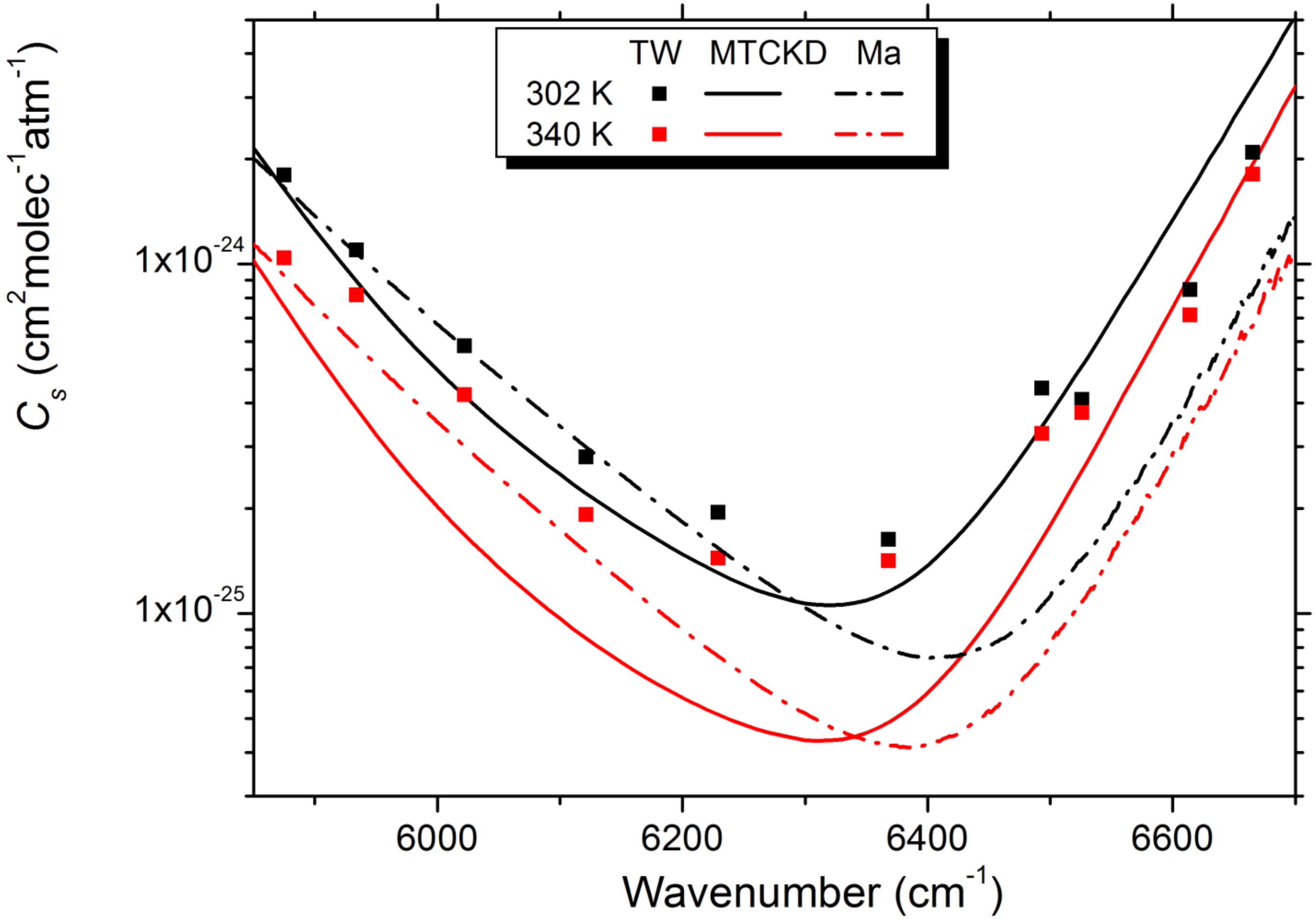


Evidence of the contribution of water adsorbed on the mirrors

$$aP + bP^2$$



Comparison with the MT_CKD model and the far-wings approach (Ma)



Conclusion & Outlooks

- We provide a complete and empirical line list between 5850-7920 cm^{-1}
- Evidence of some deficiencies in HITRAN2012

Adopted for the next edition of the GEISA database

- Water vapor continuum: Measurement of C_s + temp. dep. in the 1.6 µm window

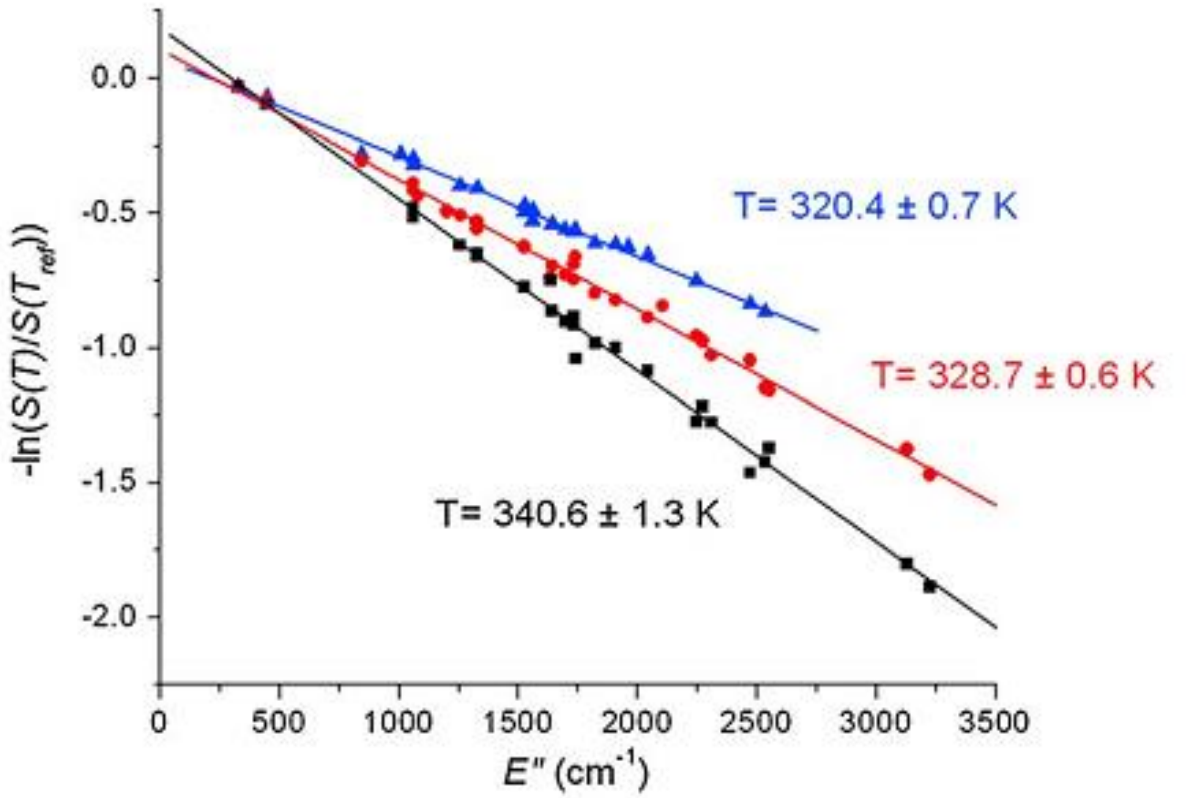
⇨ Experimental constraints for the models

Perspectives:

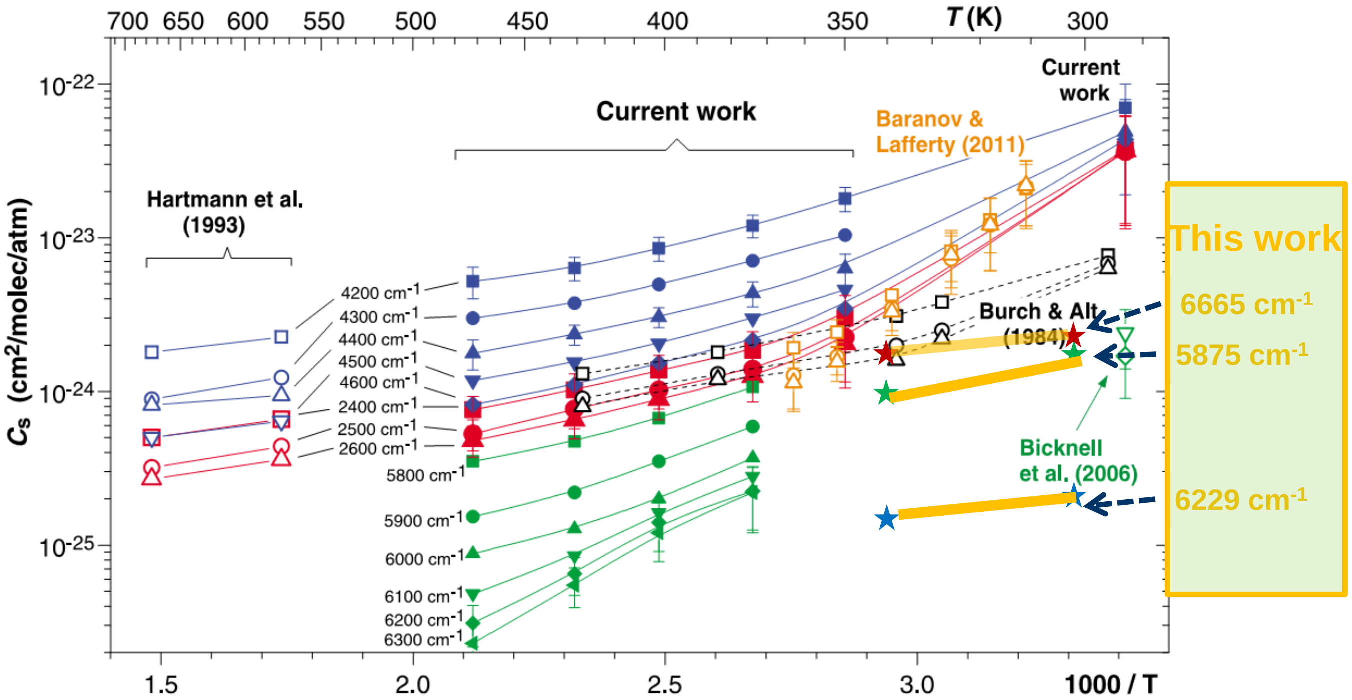
- Other TW (2.3 and 1.25 µm)
- Extend the T range + Foreign continuum

Determination of the rotational temperature in the sample

$$-\ln\left(\frac{S_{\nu_0}(T)}{S_{\nu_0}(T_{\mathrm{ref}})}\right) = E''\left(\frac{1}{kT} - \frac{1}{kT_{\mathrm{ref}}}\right) + \mathrm{cte}$$



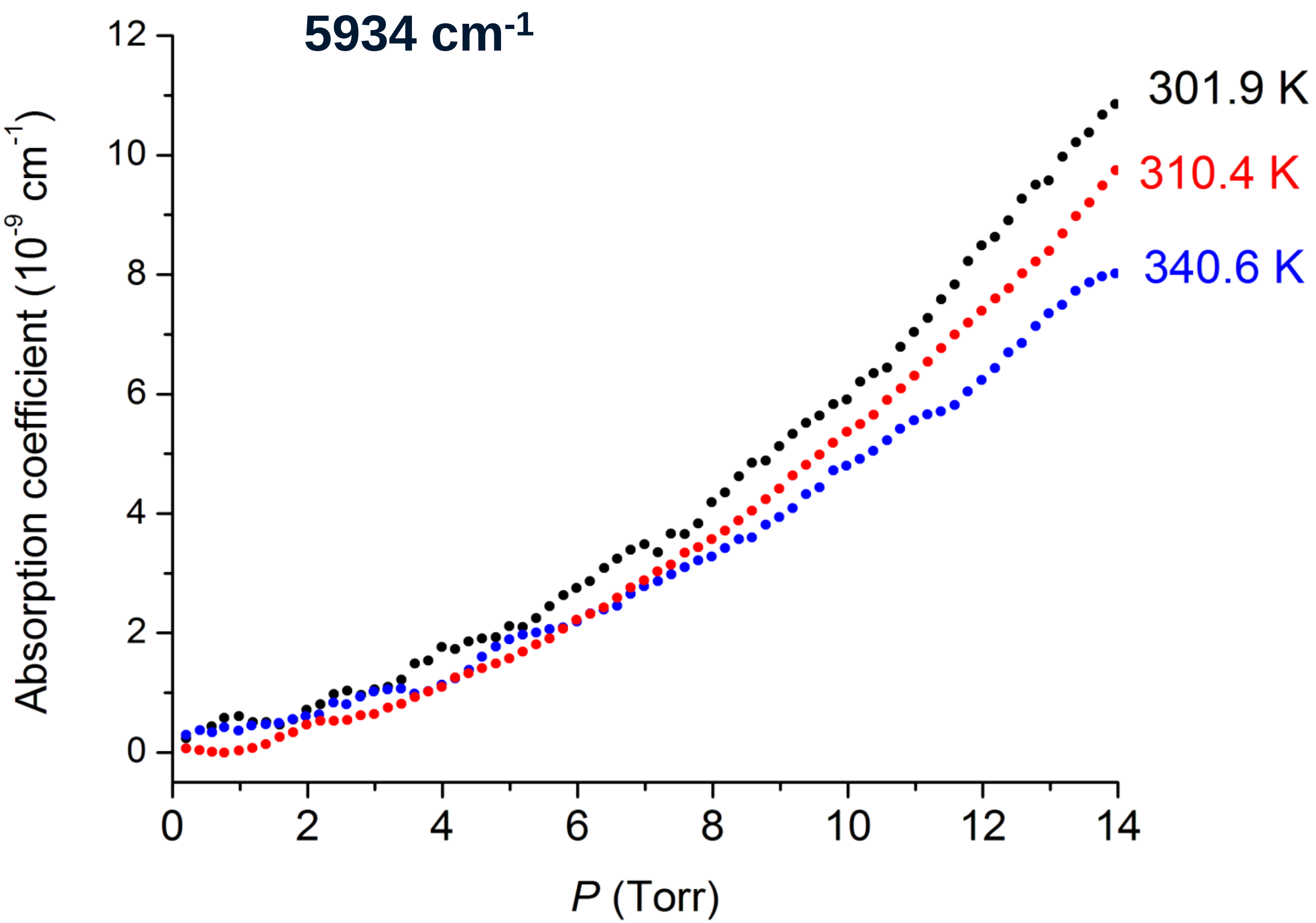
Experimental C_s cross-sections in the NIR



From Ptashnik *et al*, JGR (2011)

Temperature dependence of C_s

Challenging measurements



Temperature dependence for the dimer

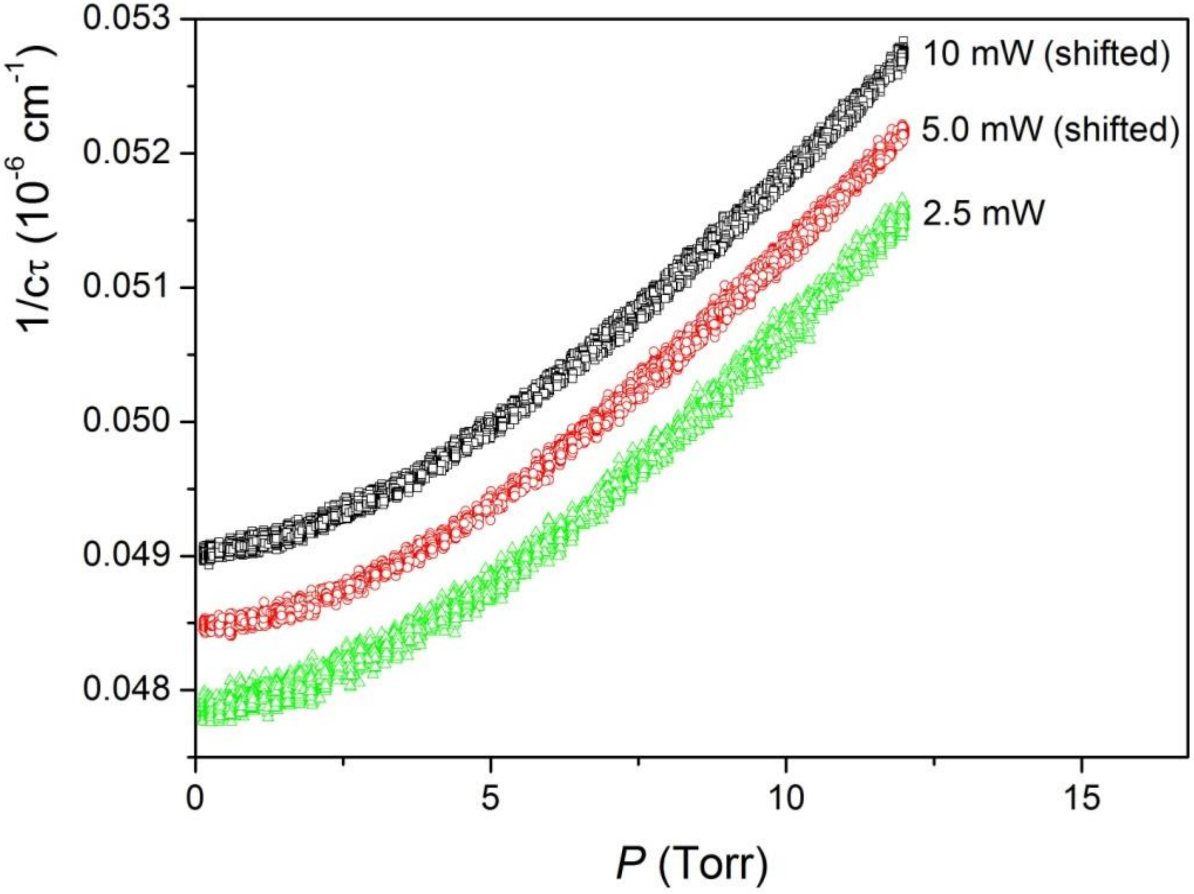
According to Vigasin JQSRT (2000):

$$C_s(\nu, T) = C_s^0(\nu) \left(\frac{T_0}{T}\right)^{n-2} \exp\left\{\frac{D_0}{k}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right\}$$

With D_0 = 1105 ± 10 cm^{-1} (dissociation energy of the dimer)

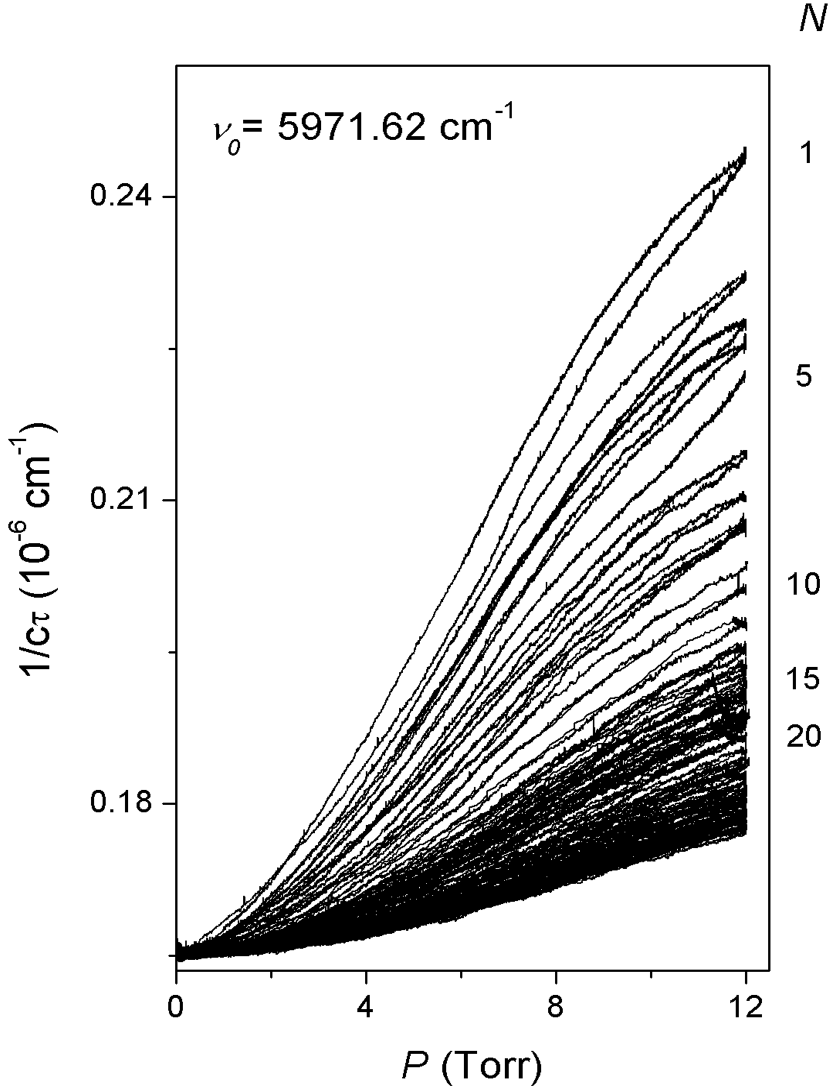
n : from 1.5 (harmonic oscillator approximation limit) to 4 (free internal rotations)

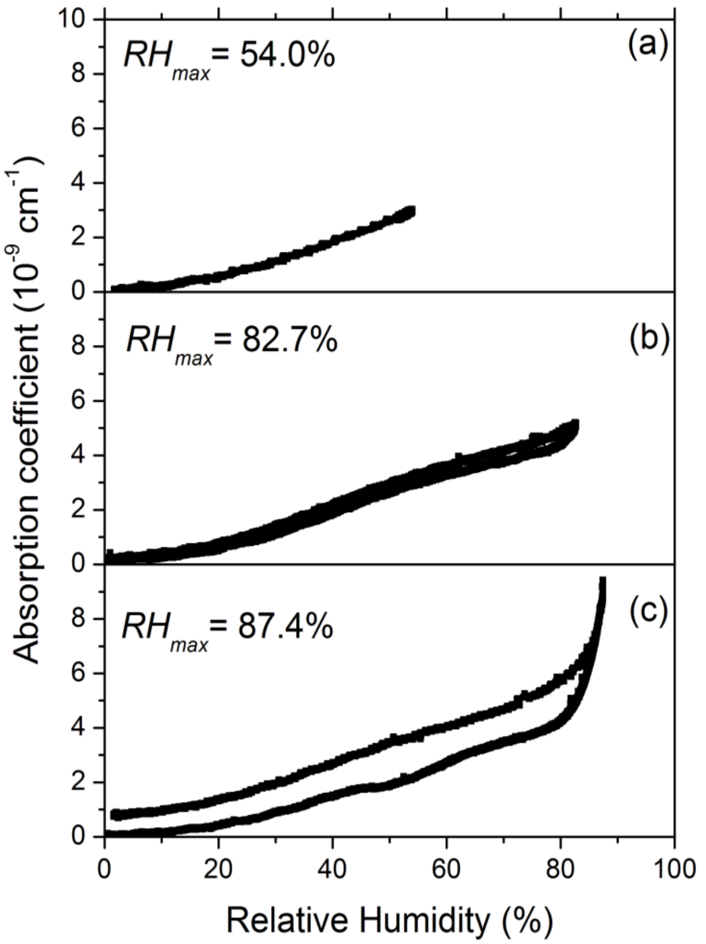
No wavelength dependence



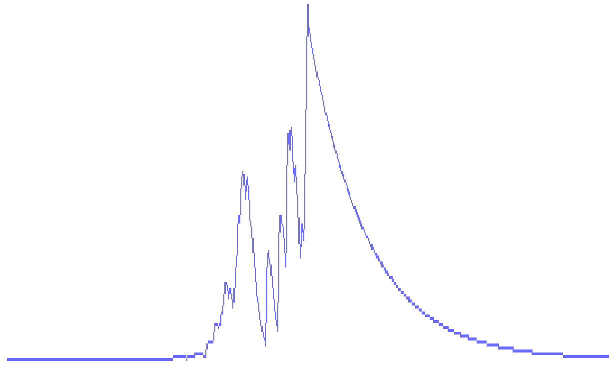
→ 0.5 W intra-cavity

Pressure dependence of the loss rate

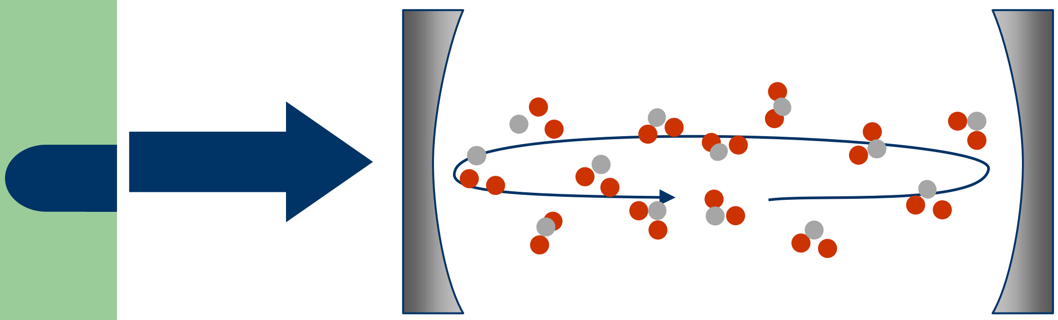


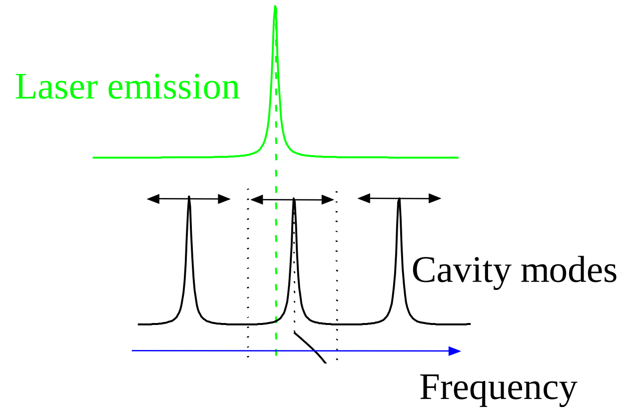


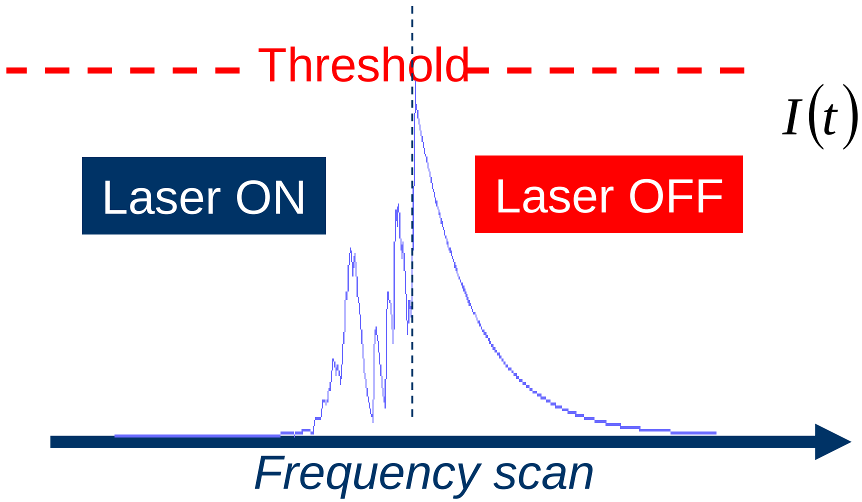
The CRDS technique



Cavity Ring Down



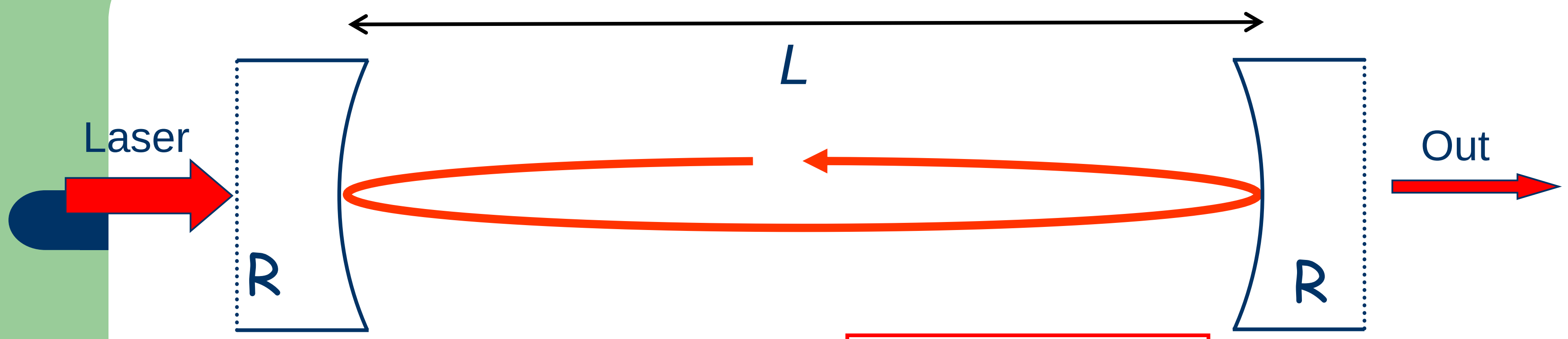




$$I(t) = I_{threshold} \exp(-t/\tau)$$

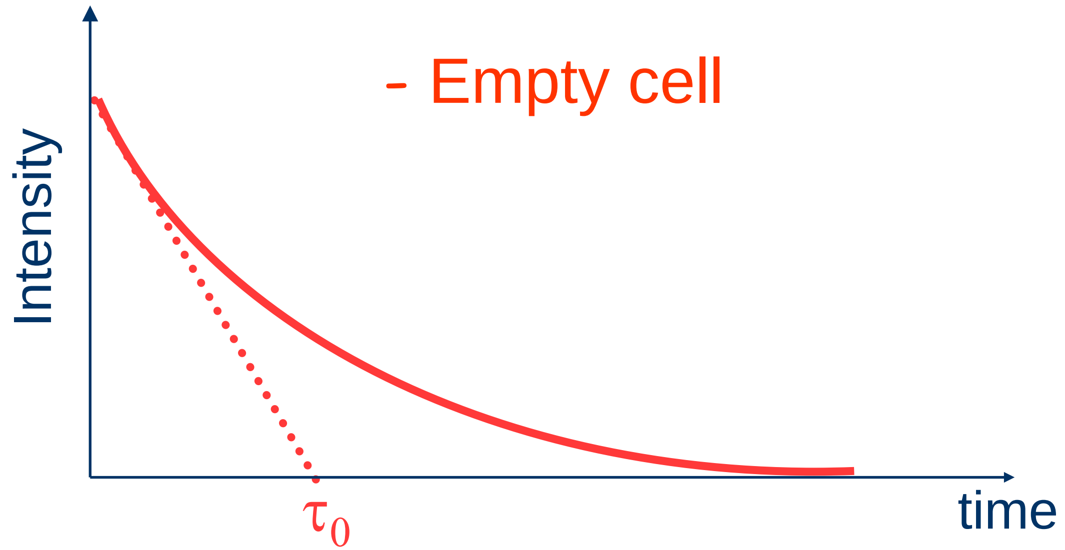
τ : ring down time

Cavity Ring Down



$R = 0.99995 \Rightarrow \tau_0 \sim 100\ \mu s$

$$\tau_0 = \frac{nL}{c(1-R)}$$



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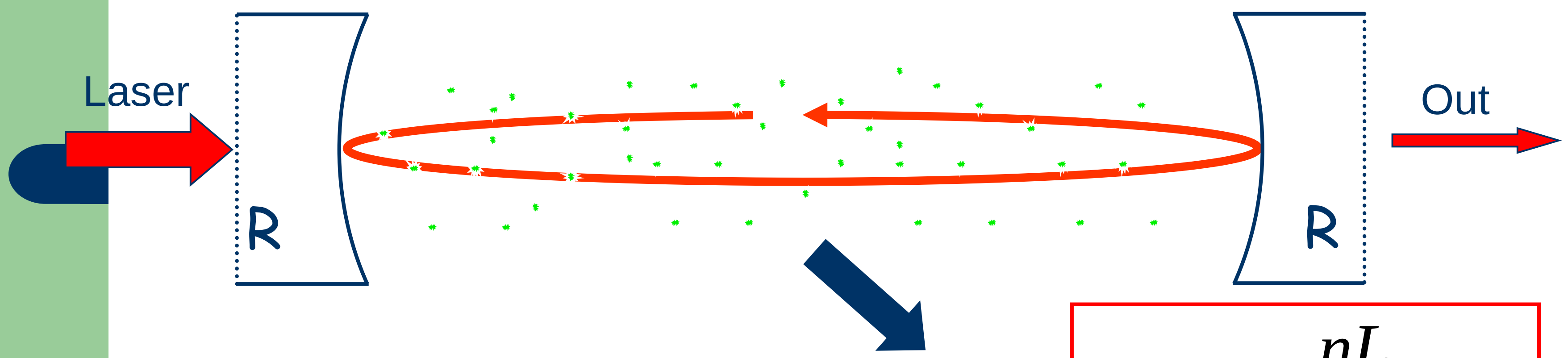
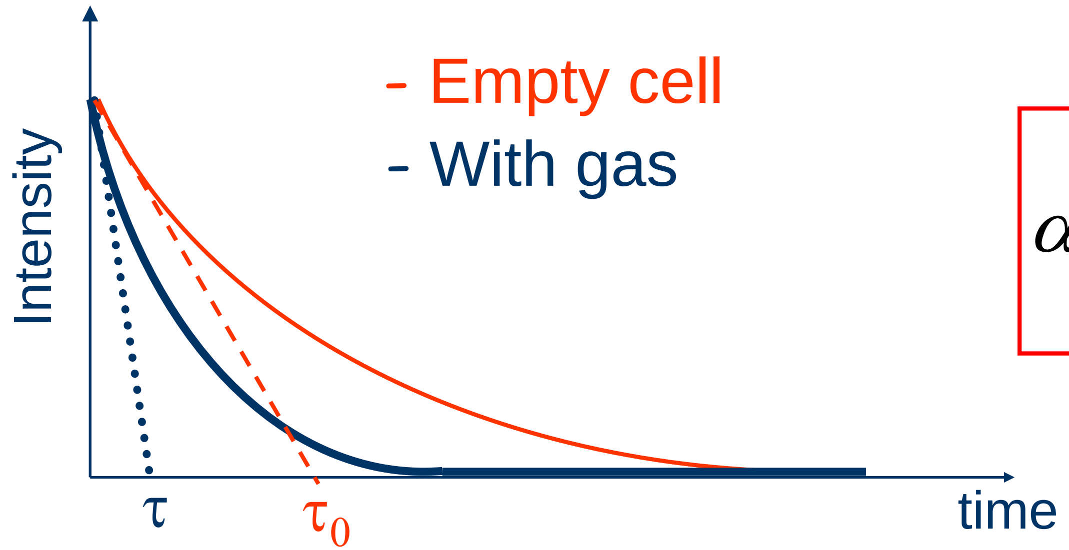


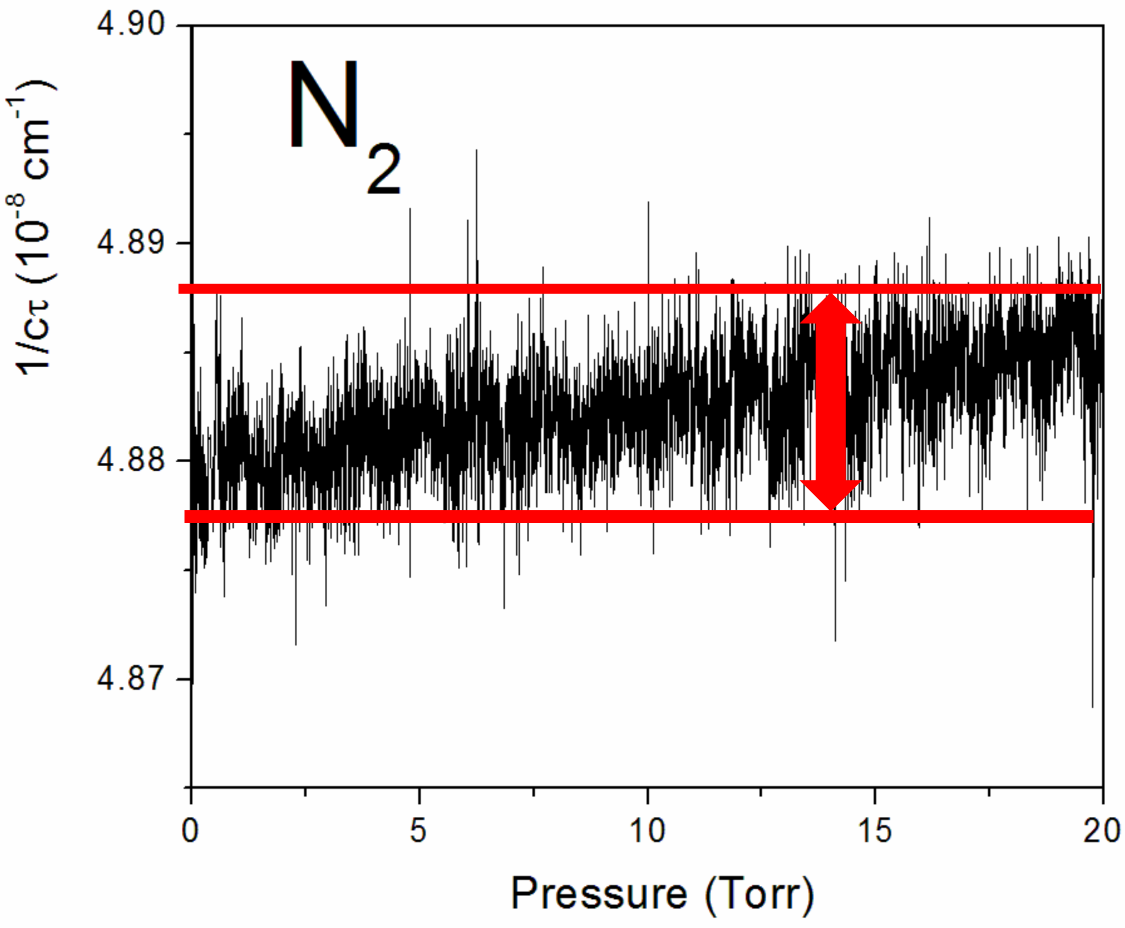
R= 0.99995 $\Rightarrow$ τ_0 ~100 µs

$$\tau = \frac{nL}{c(1 - R + \alpha L)}$$



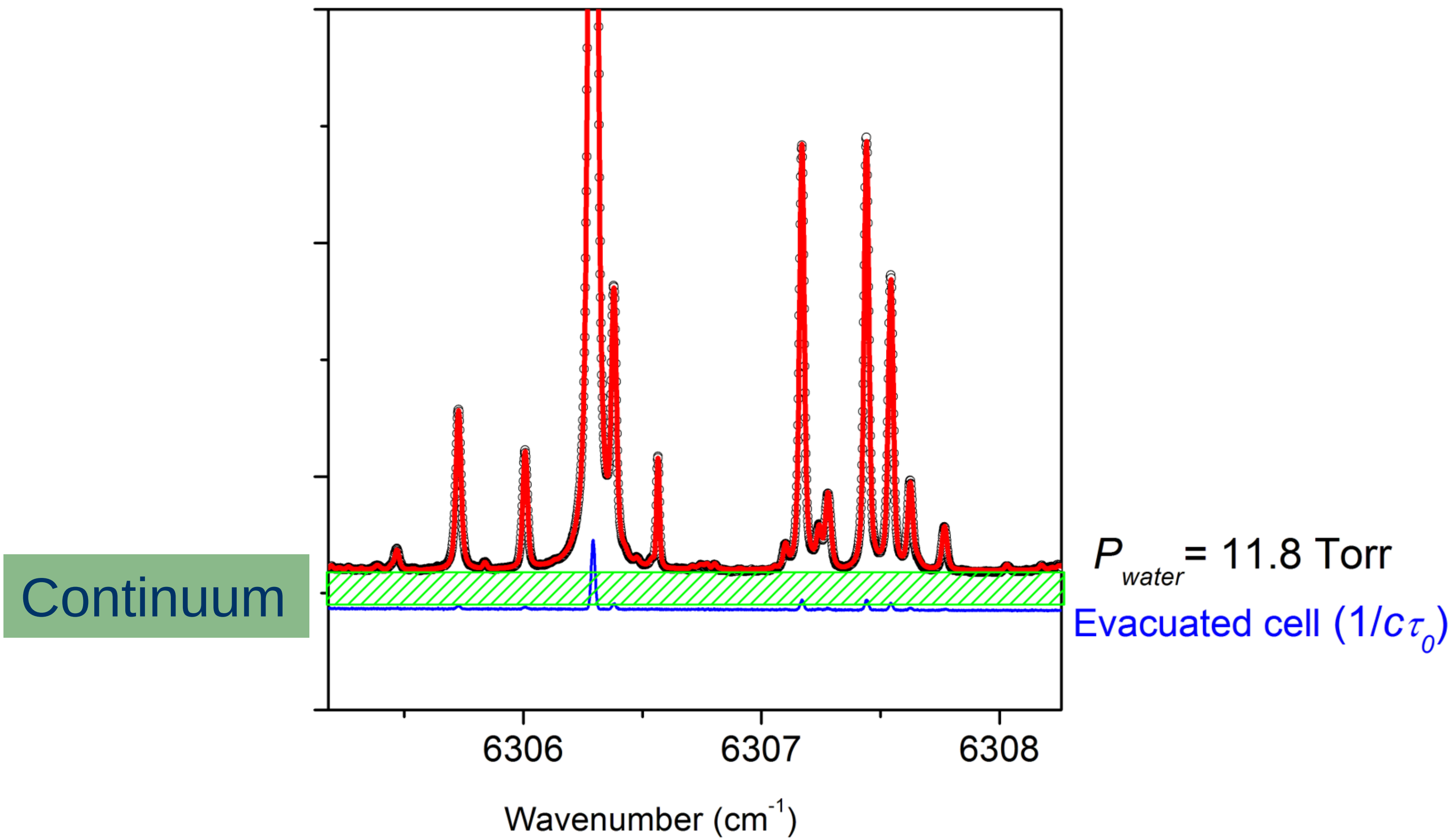
$$\alpha = \frac{1}{c}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right)$$

Base line stability

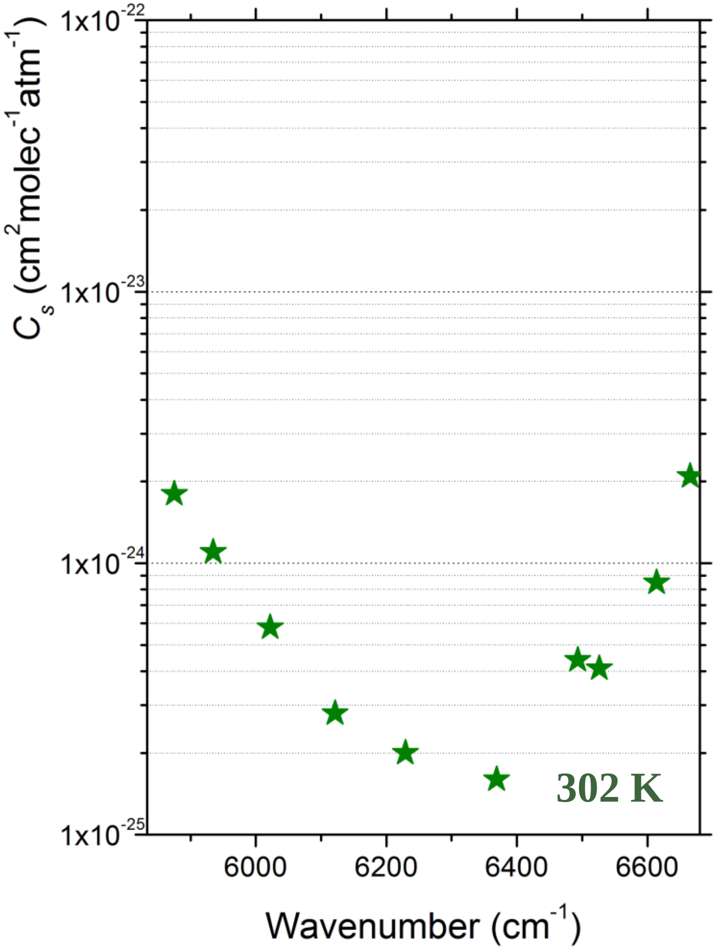


$<1 \times 10^{-10}$ cm^{-1}

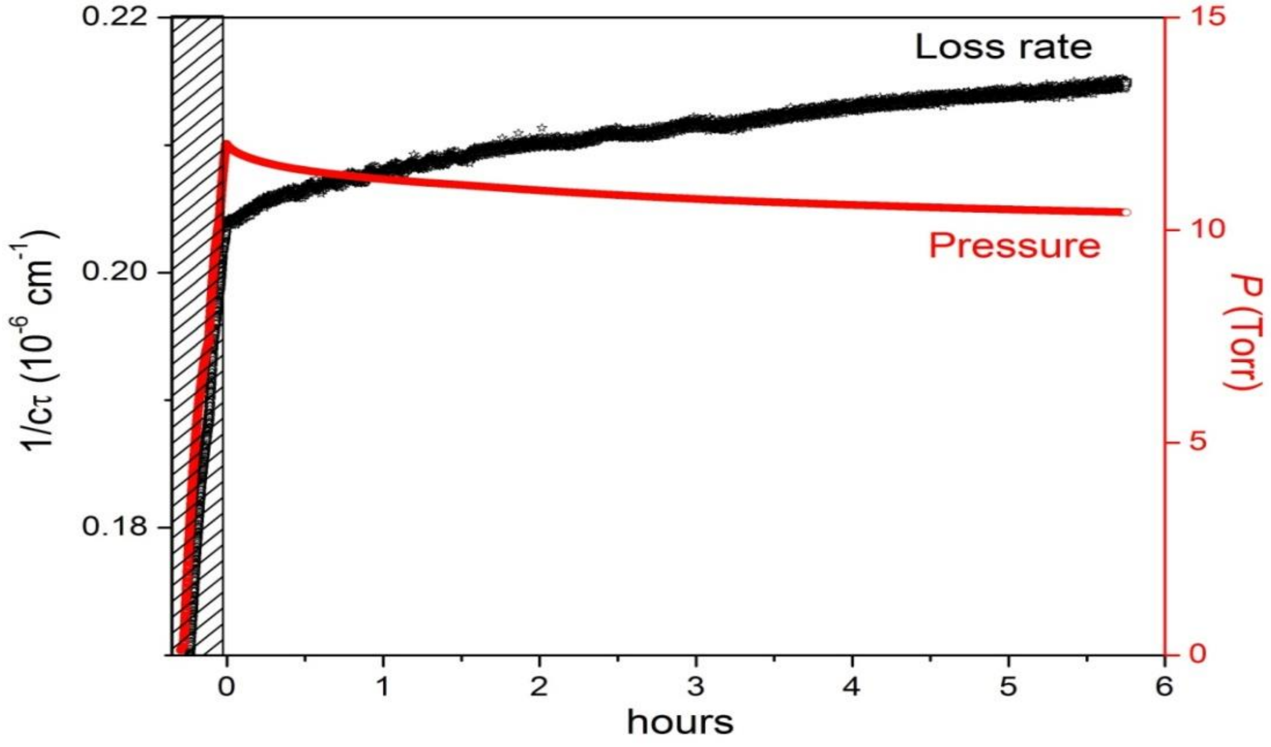
The different contributions to the extinction coefficient



Comparison with previous experimental results near RT

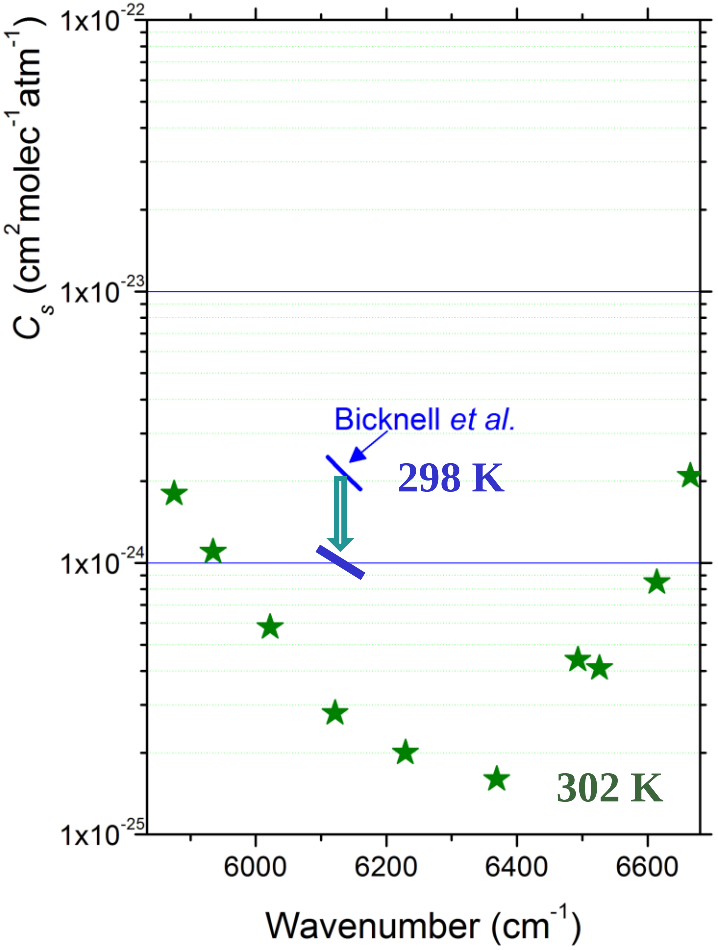


Evidence of the contribution of water adsorbed on the mirrors



$$\alpha(\nu) = \alpha_{WML} + \alpha_{WC} + \alpha_{ads}$$

Comparison with previous experimental results near RT



Bicknell *et al*
Calorimetric-interferometric method
Search for low - absorption regions in the 1.6 - and 2.1 -µm atmospheric windows.
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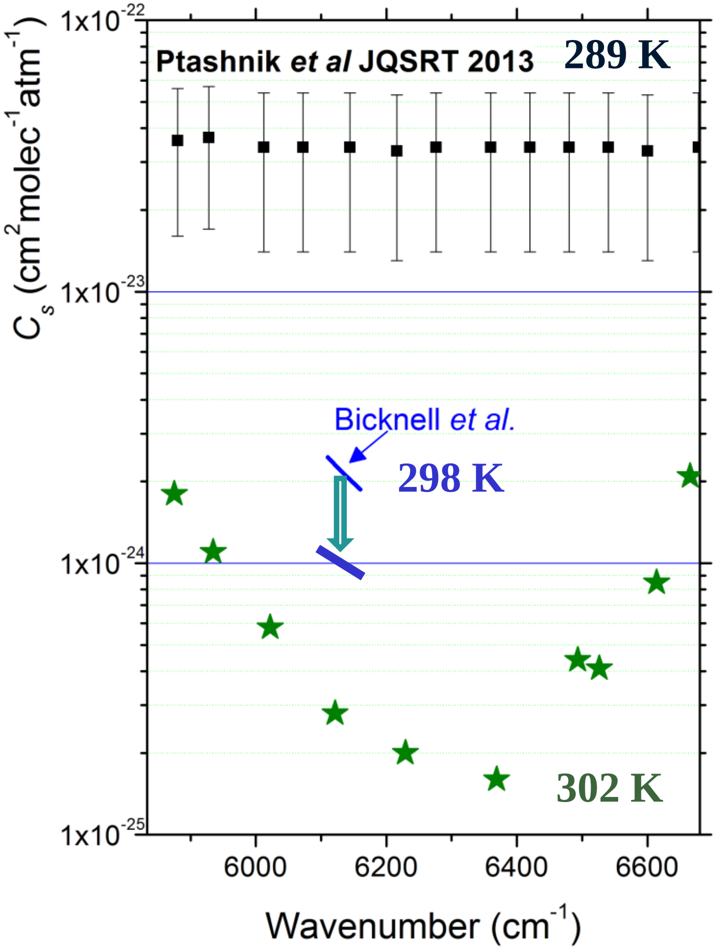

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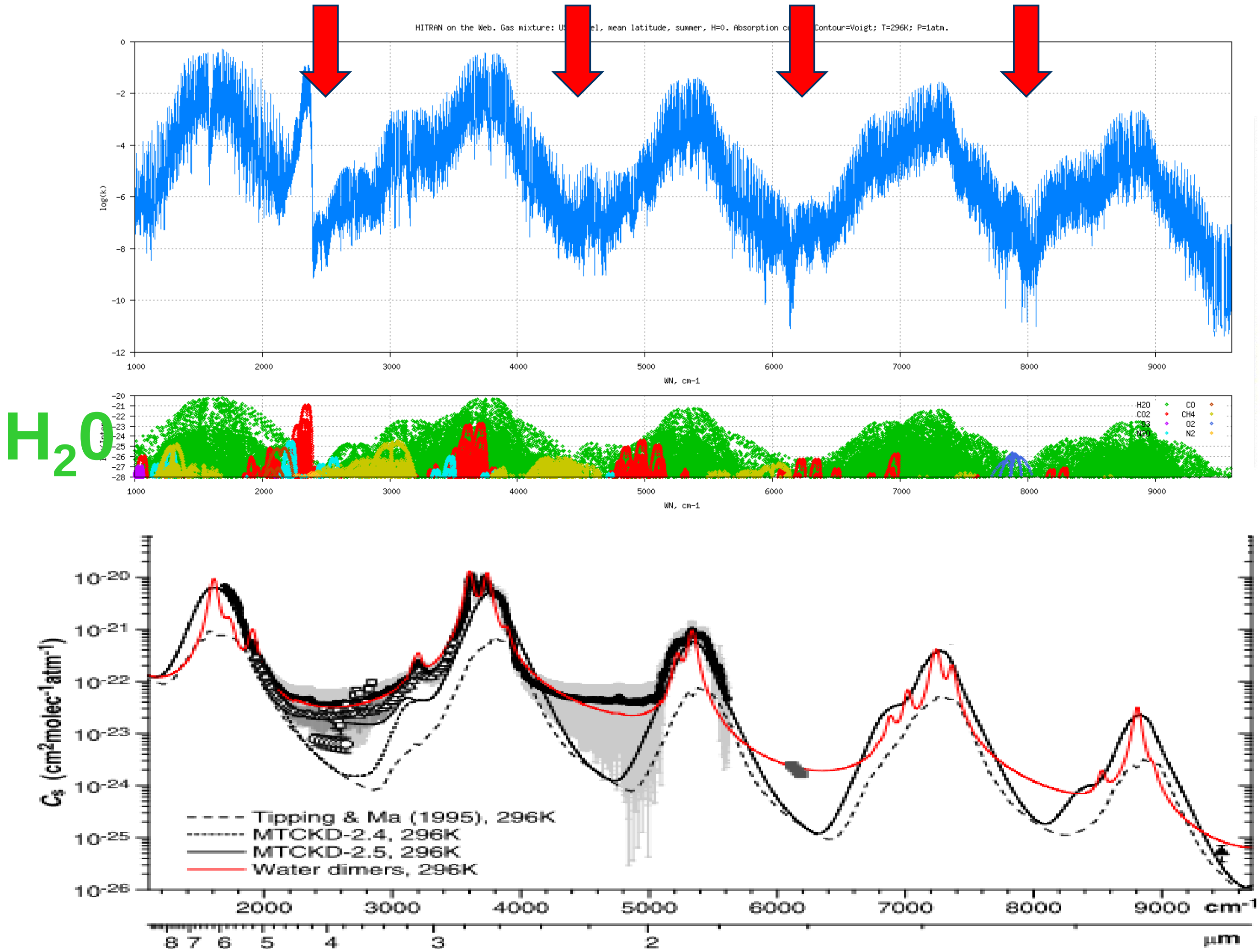
Introduction

Remote sensing of the Earth's atmosphere requires an accurate characterization of the transparency windows



Water vapor absorption

=

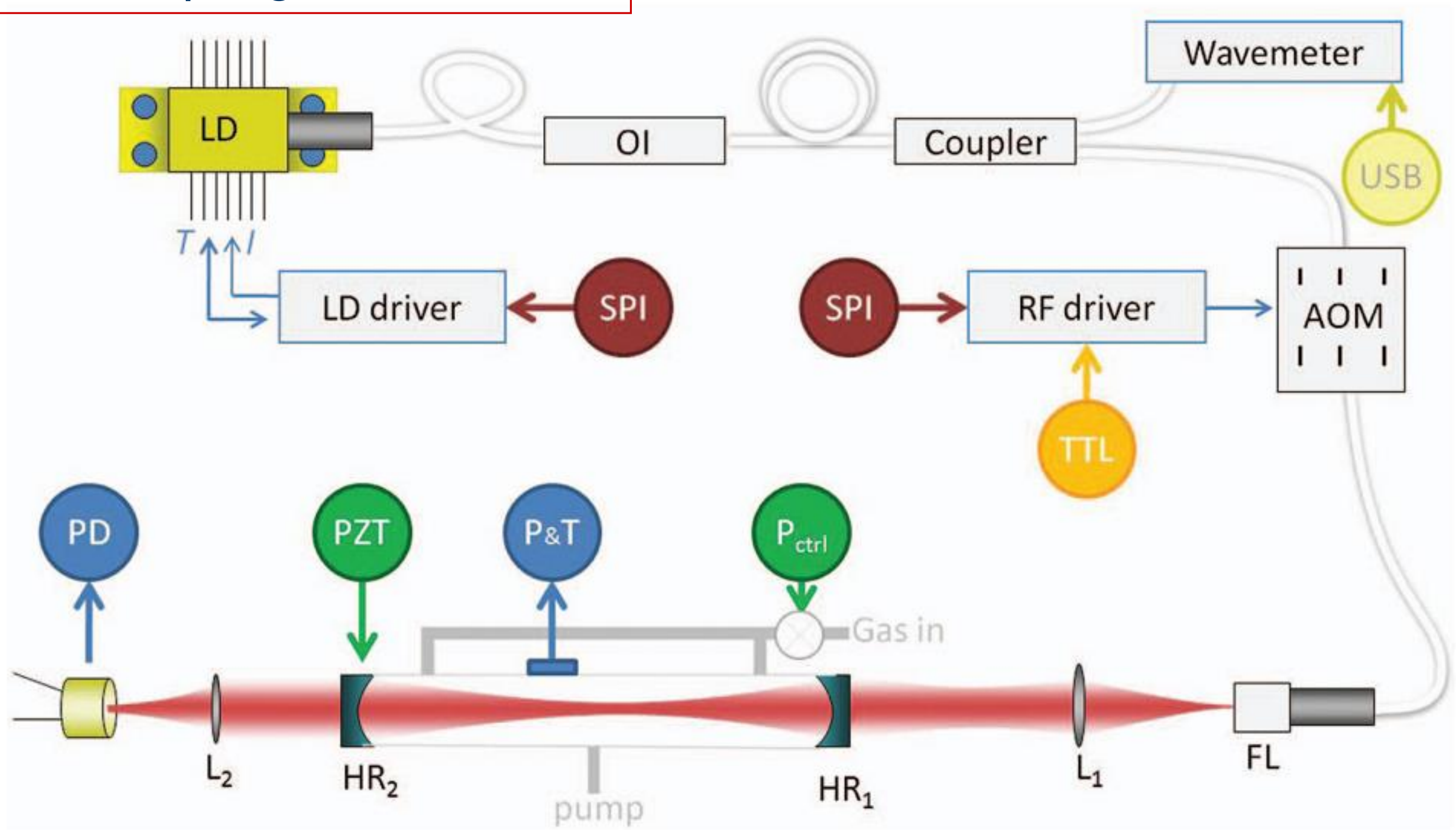
Local lines absorption

+

Continuum absorption

Experimental CRDS setup

T_{diode}: -10°C – 60°C (~ 35 cm^{-1})
Spectral sampling: 2×10^{-3} cm^{-1}



80 DFB laser diodes
6nm/diode

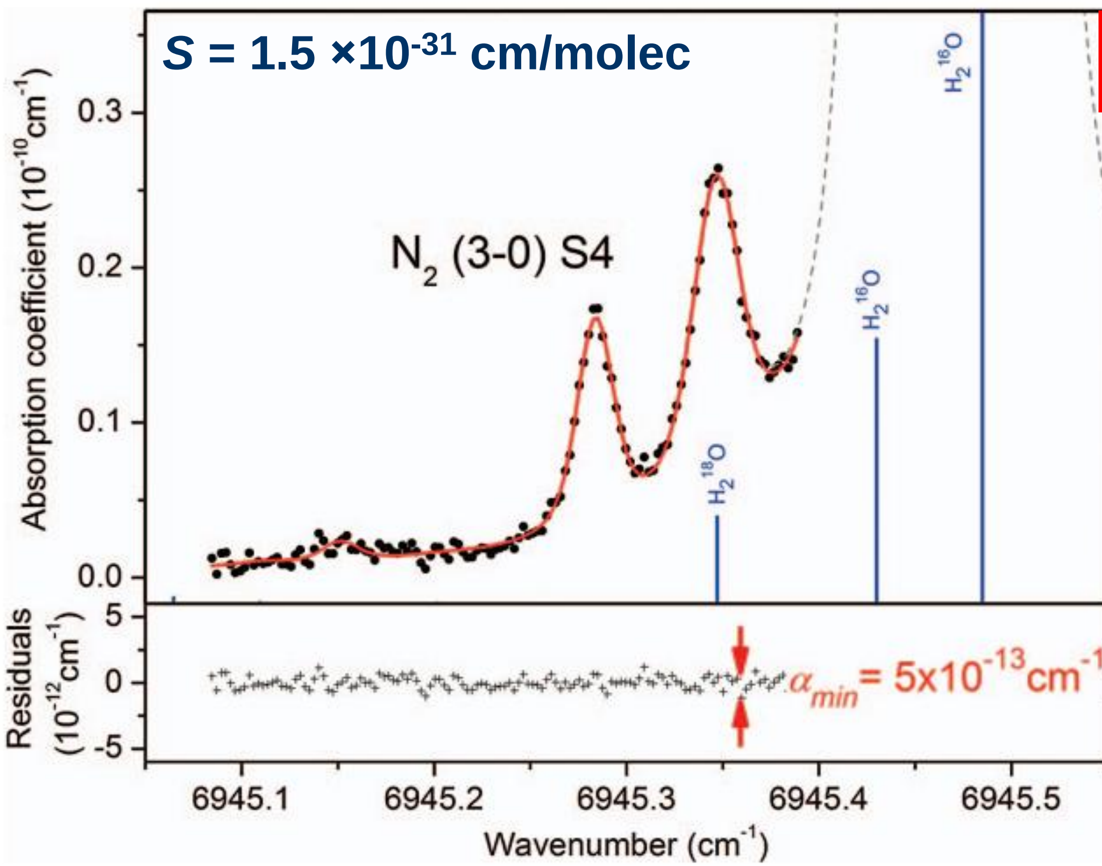
+ ECDL

→ Large spectral coverage
5850 – 8330 cm^{-1} (1.72-1.20 µm)

An ultra-sensitive technique…

Typical noise level in routine: α_{min}~5×10^{-11} cm^{-1}

2% light attenuation
(~400 000 km)

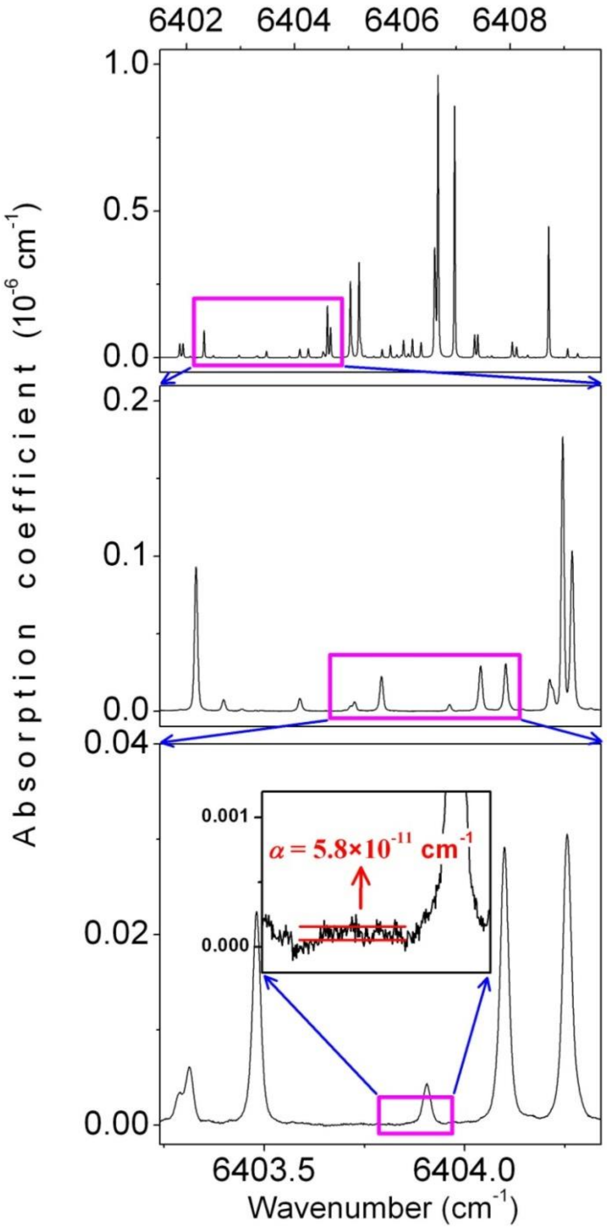


$\alpha_{min}=5\times10^{-13}$ cm^{-1}

Kassi and Campargue, JCP (2012)

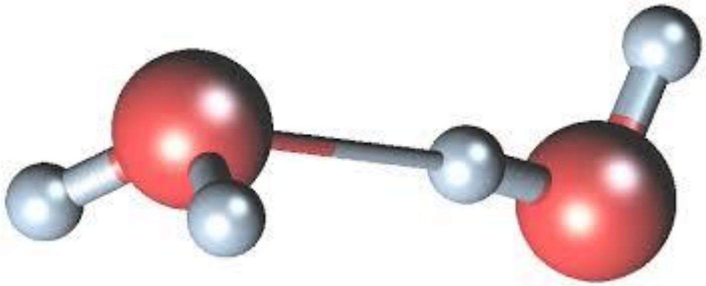
… with a high dynamics

Dynamics >
4 orders of magnitude



Origin of the continuum?

Water dimer = two weakly bounded water molecules



Far-wings of the monomer absorption lines

Collision-induced absorption bands (CIA)