Some (!) Fundamentals of Atmospheric Radiation
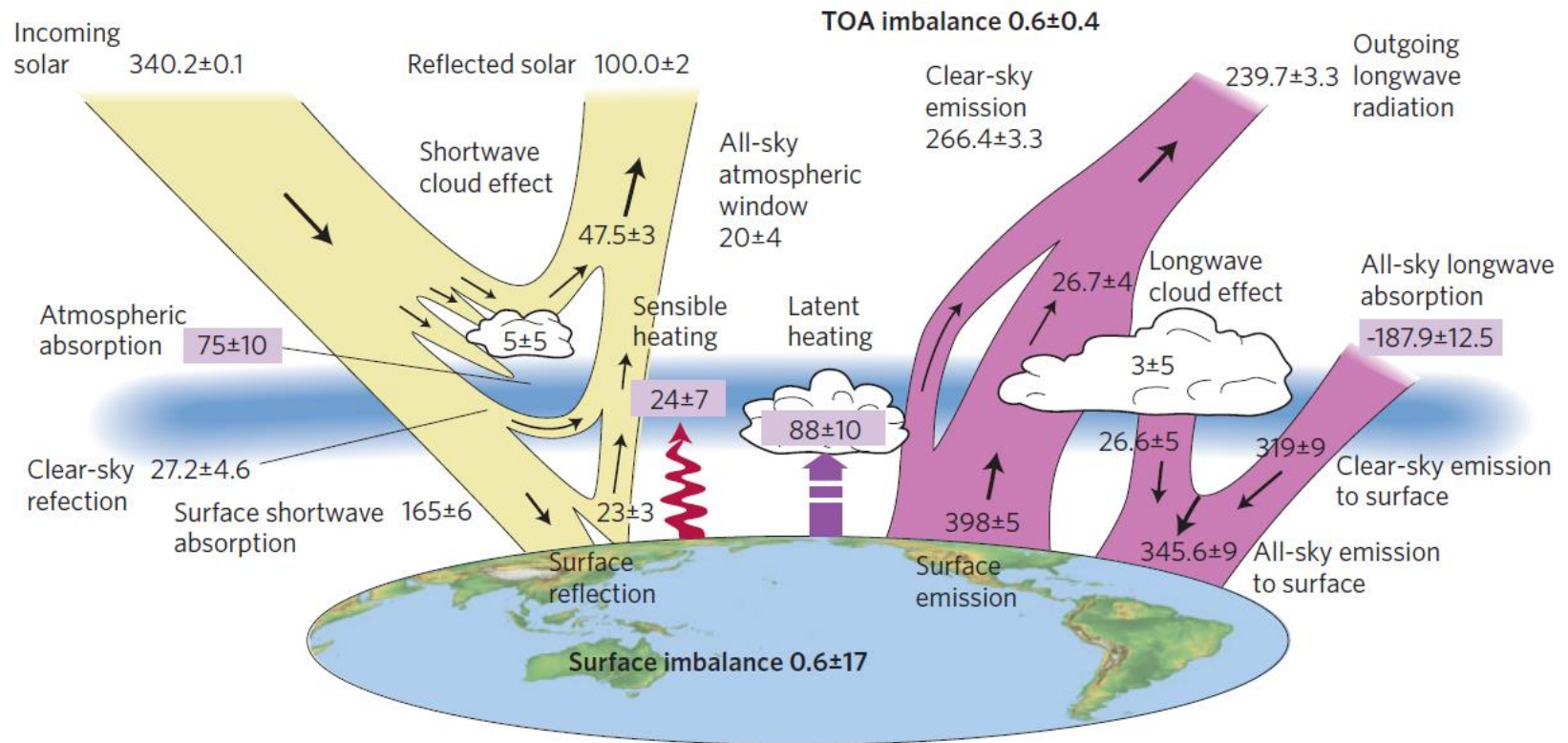
Keith Shine

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Department of Meteorology, University of Reading, UK

University of Reading

Modern (global and annual averaged) Earth energy budget

Stephens et al. (2012), Nature Geoscience 10.1038/NGEO1580

Contents

- Incoming solar radiation
- A brief introduction to molecular spectroscopy and the HITRAN database
- Some of my group's work 1: water vapour continuum in the near-infrared
- Some of my group's work 2: incoming solar spectral radiance in the near infrared

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Incoming solar radiation

- Measured Total solar irradiance (TSI) S_o (used to be known as the *Solar Constant*) at solar minimum is about 1361 ± 0.5 W m^{-2}. This implies that the Sun is emitting as a black body at a mean temperature, T_{sun}, of about 5760 K

www.pmodwrc.ch
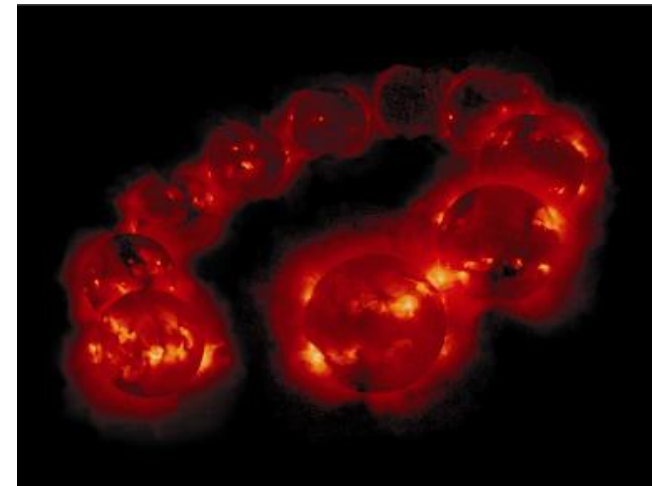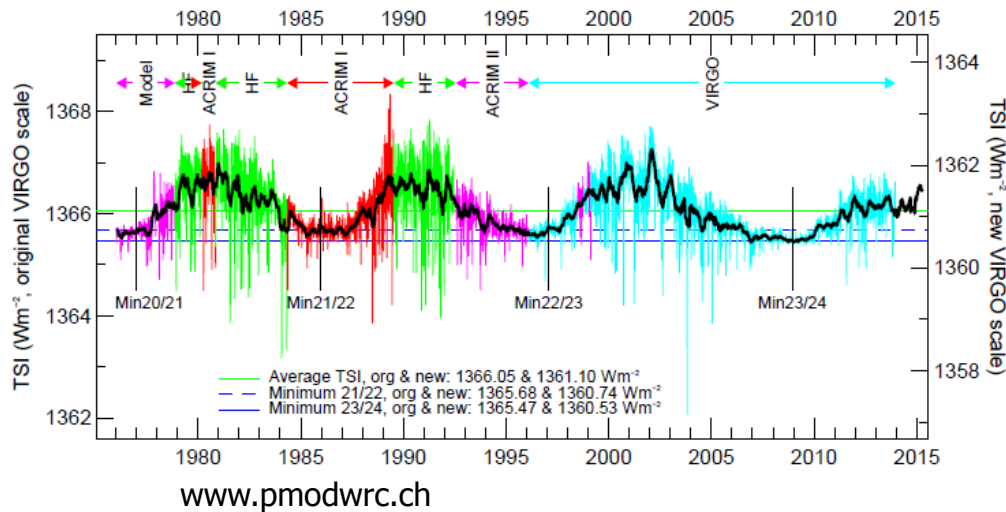
- Will show later that precision of total solar irradiance does *not* translate into good knowledge of the spectral distribution of incoming solar radiation

Incoming solar radiation (continued)

Average solar irradiance absorbed by Earth is

$$\frac{S_o \pi . r_e^2}{4\pi . r_e^2}(1-\alpha_p) = \frac{S_0}{4}(1-\alpha_p) = 240 \; W \, m^{-2}$$

where α_p the *planetary albedo,* (by clouds, gases, aerosols and the surface) and r_e is the Earth's radius. Satellite *observations* indicate α_p =0.3
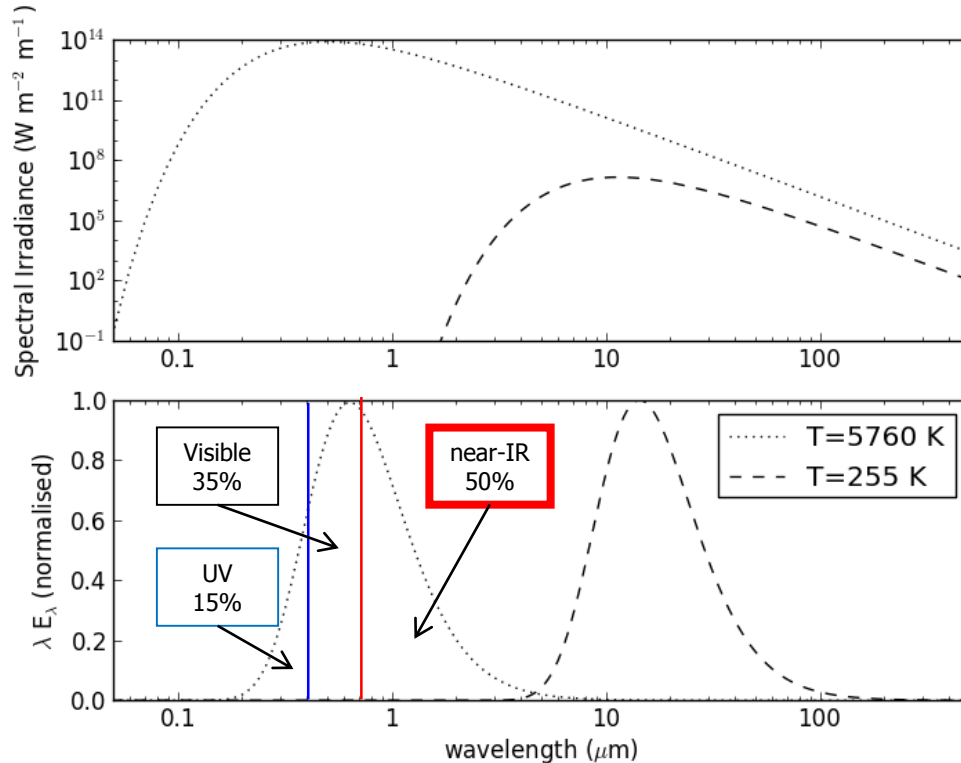
Given a long term balance between the energy *absorbed* from the Sun and the energy *emitted* to space by the Earth-atmosphere system and *assuming* (for now!) that the Earth-atmosphere system emits as a black body to space at a temperature T_e *then*

$$\frac{S_o}{4}(1-\alpha_p) = \sigma T_e^4$$

$$T_e \;\; = \;\; 255K.$$

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Spectral variation of incident/emitted radiation

Planck function describes the spectral variation of radiation emitted by a black body:

$$E_\lambda = \frac{\pi c_1 \lambda^{-5}}{(\exp(c_2/\lambda T) - 1)}$$

[The bottom plot is plotted so that equal areas give equal irradiances, and shows that the amount absorbed by Earth is about the same as the amount emitted by Earth]
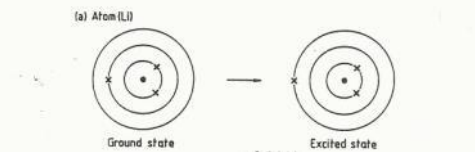
The top plot shows the Planck function for the Sun and Earth temperatures (in reality they are not black bodies

The Sun's emission is diluted by the inverse square law and the amount *absorbed* per unit area of Earth requires multiplication by $(1-\alpha_p)/4$. Bottom plot show the effect of both of these factors
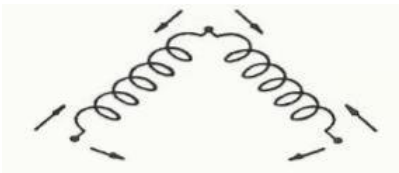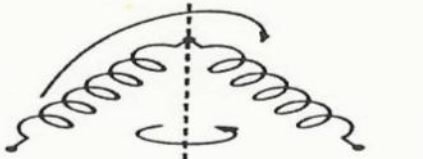
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Absorption and emission by atmospheric gases

Characteristic spacing between energy levels (and hence the wavelength of absorption/emission) depends on the type of excitation

It takes, in relative terms, a lot of energy (and hence a high frequency/small wavelength) to lift a molecule's electron into an excited state, but less energy to get it to rotate faster

Transition		wavelength and wavenumber range
Electronic		0.1–1 µm (vis, UV) (10,000 - 100,000 cm^{-1})
Vibration		1–20 µm (near-IR and IR) (10,000 – 500 cm^{-1})
Rotation		20–1000 µm (far IR and micro-wave); (500 – 10 cm^{-1})

Cartoons from Richards and Scott (1985) Structure and Spectra of Molecules, John Wiley

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Absorption mechanisms

For a molecule to absorb or emit a photon is it must possess a electric (or magnetic) dipole (either a permanent one (e.g. H_2O) or as a result of vibration (e.g. CO_2))

The most abundant molecules (nitrogen and oxygen) do not have an electric dipole, and so play a more minor role in atmospheric radiation
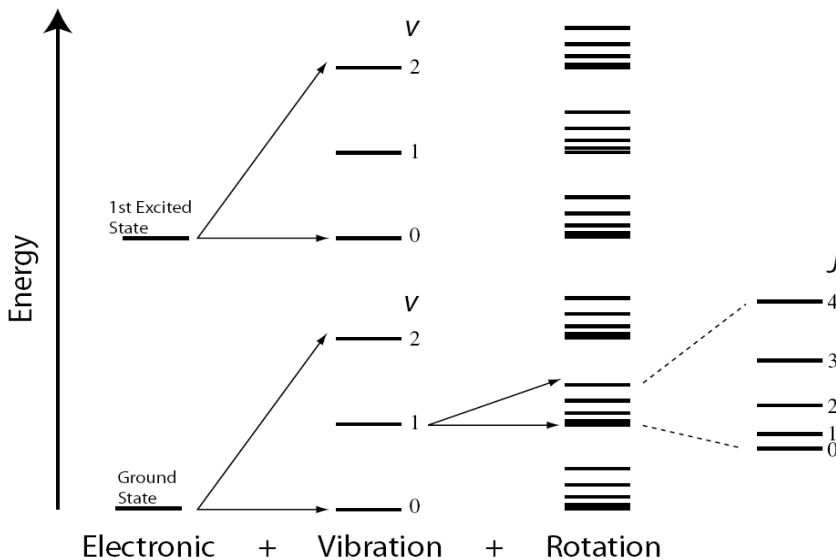
Molecules can possess (and change) simultaneously electronic/vibration/rotation– the large number of possible vibration-rotation transitions is what leads to the complexity in the molecular spectra

Petty, G. A First Course in Atmospheric Radiation, Sundog Publishing 2004

Vibration-rotation spectra

Diatomic (N_2, O_2, CO)

Linear triatomic (CO_2, N_2O)
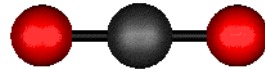
Symmetric stretch v_1	Bending v_2	Asymmetric stretch v_3

Nonlinear Triatomic (H_2O, O_3)
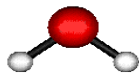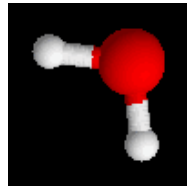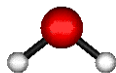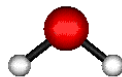
Symmetric stretch v_1	Bending v_2	Asymmetric stretch v_3

When N_2 and O_2 vibrate, there is no change in dipole moment (except when an electric field is imposed from outside, as in Rayleigh scattering)

CO_2 has no permanent dipole and hence no pure rotation spectrum; it *can* possess a dipole moment when it vibrates and therefore have a vibration - rotation spectrum

Water vapour and ozone have a permanent dipole and hence a pure rotation spectrum as well as a vibration-rotation spectrum

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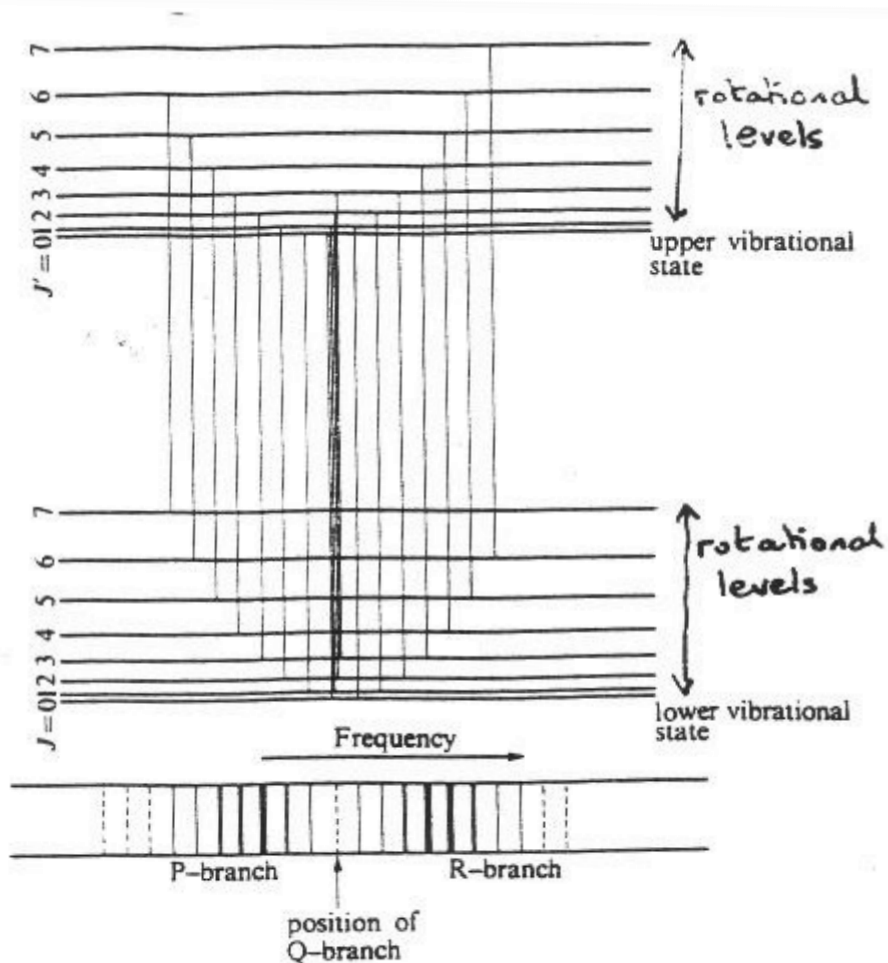# Vibration-rotation spectra (continued)

Fig. 17.13. The formation of P, Q, and R branches.
from Atkins, P.W. (1982) Physical Chemistry (Oxford)

Because
- the rotational energy levels are not equally spaced in energy and
- not all molecules start at the same energy level

this leads to molecules possessing absorption *bands* where there are lots of transitions in a relatively narrow wavenumber region

Line Broadening

(a) without broadening

Absorption · Wavelength

(b) with broadening

Absorption · Wavelength
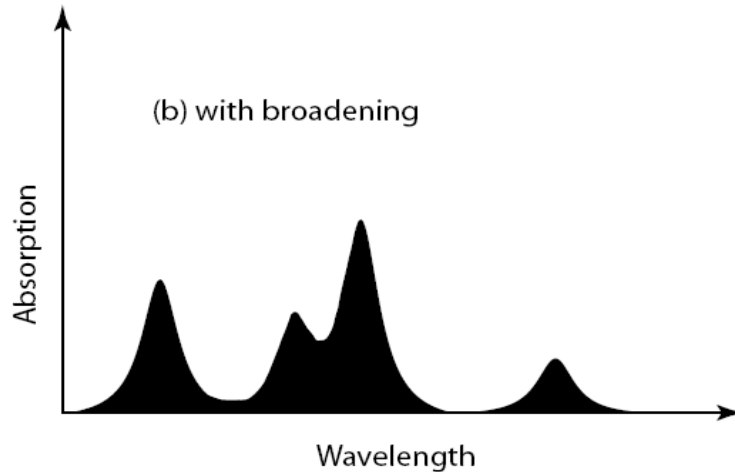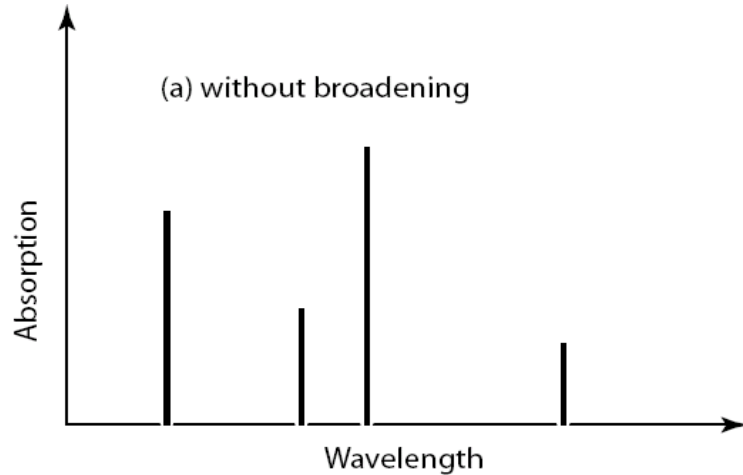
Petty 2004

Transitions are not at discrete wavelengths because of line broadening. In the atmosphere this is dominated by

•*Collision (or pressure) broadening*, due to the collisions between "air" molecules and emitting/absorbing molecules

•*Doppler broadening*, due to relative motion of absorbing/emitting molecules

In some cases, this broadening, can be so large, relative to the line spacing, that it is hard to actually see the individual lines, and we have more of a *continuum* of absorption

Vibration-rotation spectra

Carbon Monoxide O — C

Nonlinear Triatomic (H_2O, O_3)

Symmetric stretch
ν_1

Bending
ν_2

Asymmetric stretch
ν_3

Petty 2004

Zenith Transmittance due to H_2O
Wavelength (μm)

wavenumber
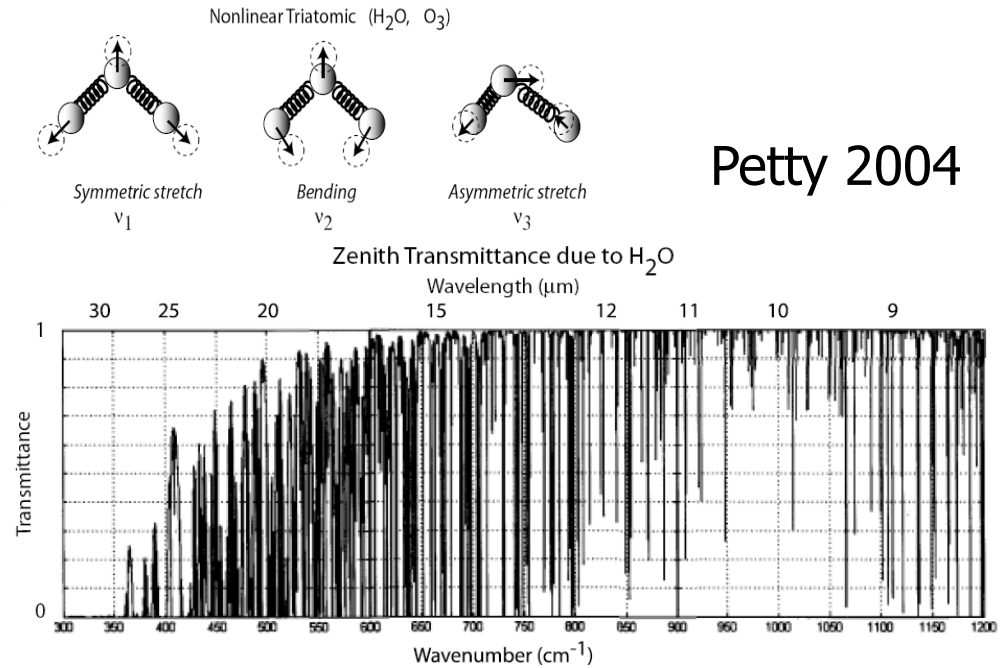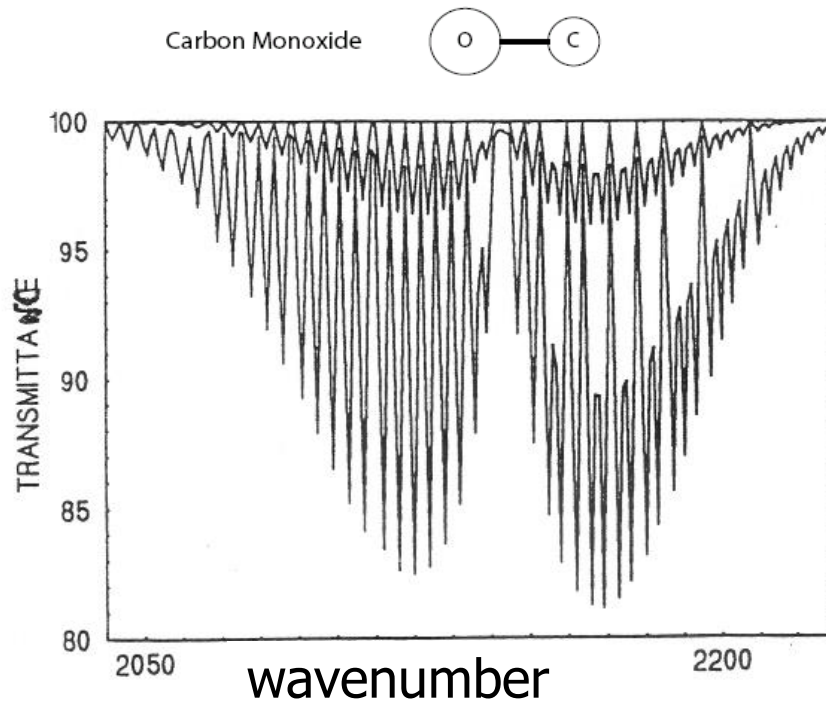
Figure 18 The 4.65 micron fundamental of carbon monoxide is shown for paths from space to 0 and 10km altitude. from Kyle, T.G. (1991) Transmission, Emission, Scattering. Pergamon.

Spectra for a simple molecule – carbon monoxide, … regular equally spaced lines

By contrast, water vapour has so many modes of vibration and rotation, that its spectrum looks almost random

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Major absorption bands – carbon dioxide
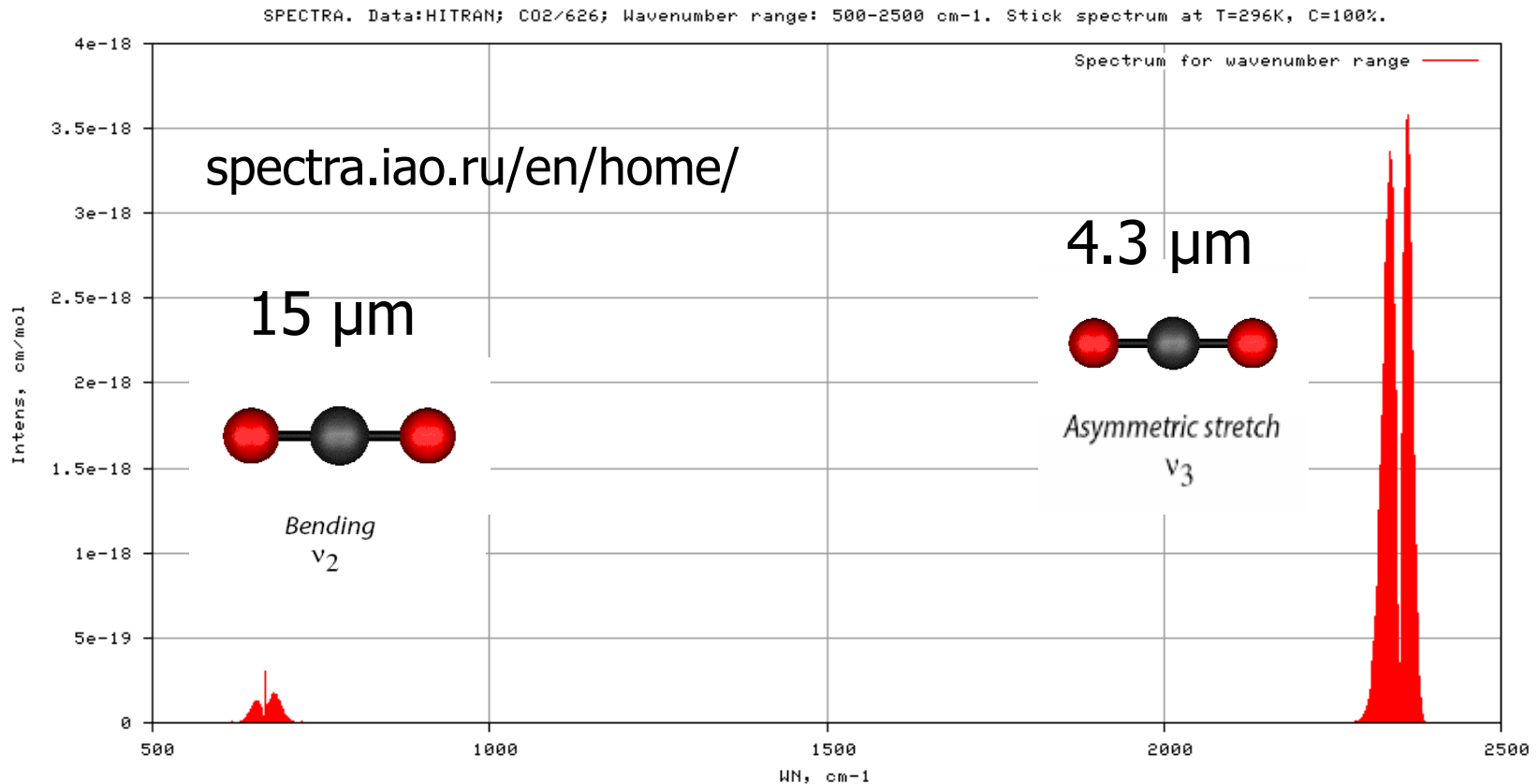
CO_2 has a strong band at 15µm (bending) and an even *stronger* band at 4.3 µm which is much less important for atmospheric radiation, as it falls in the "gap" between the solar and terrestrial Planck functions

Major absorption bands – water vapour

SPECTRA. Data:HITRAN; H2O/161; Wavenumber range: 0.072059-8000 cm-1. Stick spectrum at T=296K, C=100%.

Pure rotation band

6.3 μm

010

spectra.iao.ru/en/home/

combinations of vibrations …

020, 100, 001   110, 011   021 ,200, 101
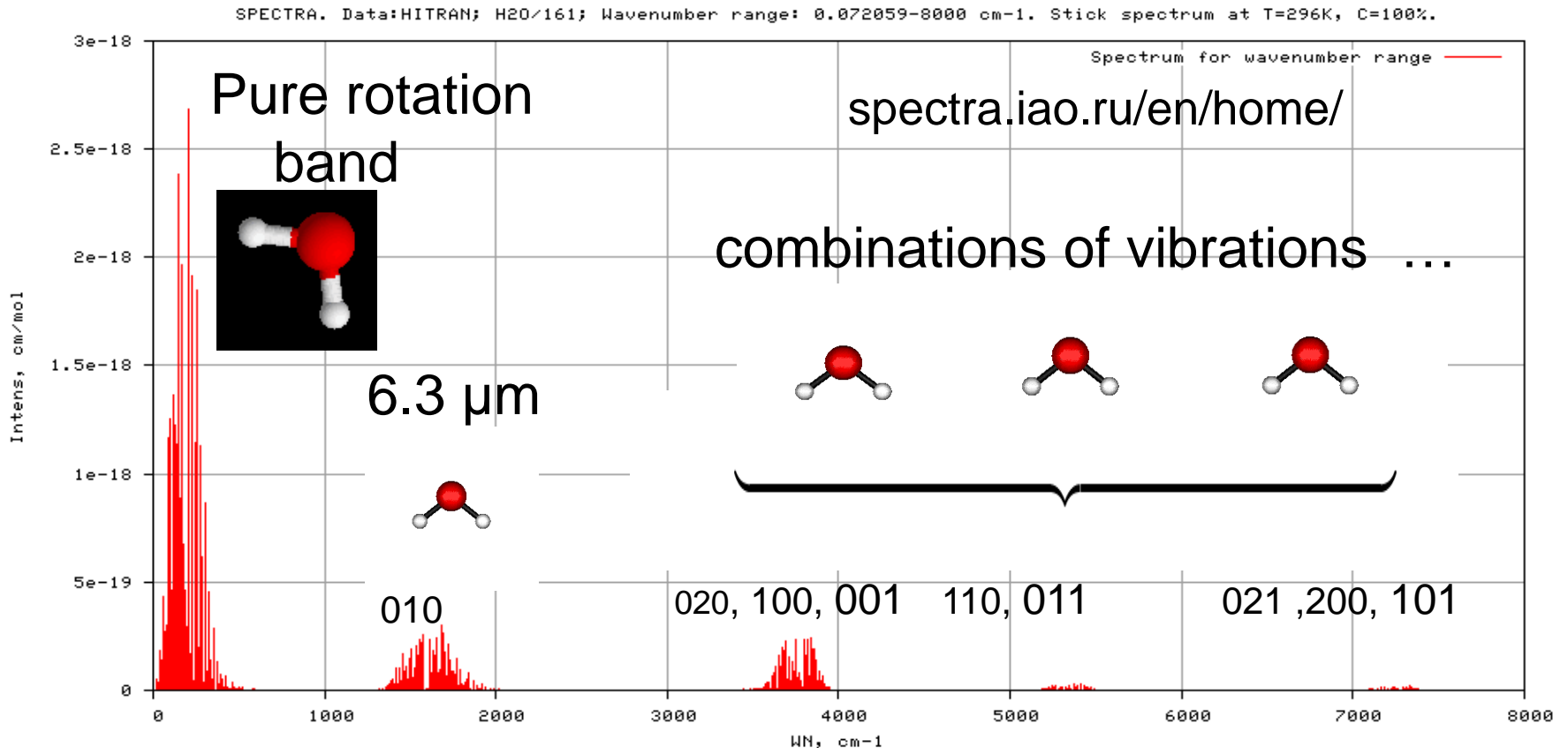
More complicated structure is because water vapour absorption is due to many modes of rotation and vibration that overlap

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Other molecules

The plot shows the transmittance of a vertical path through the atmosphere for a range of gases

This includes the strength *and* abundance of the molecules – note that even some apparently weak bands in earlier sliders, are still completely absorbing over atmospheric paths

ZENITH ATMOSPHERIC TRANSMITTANCE

Petty 2004
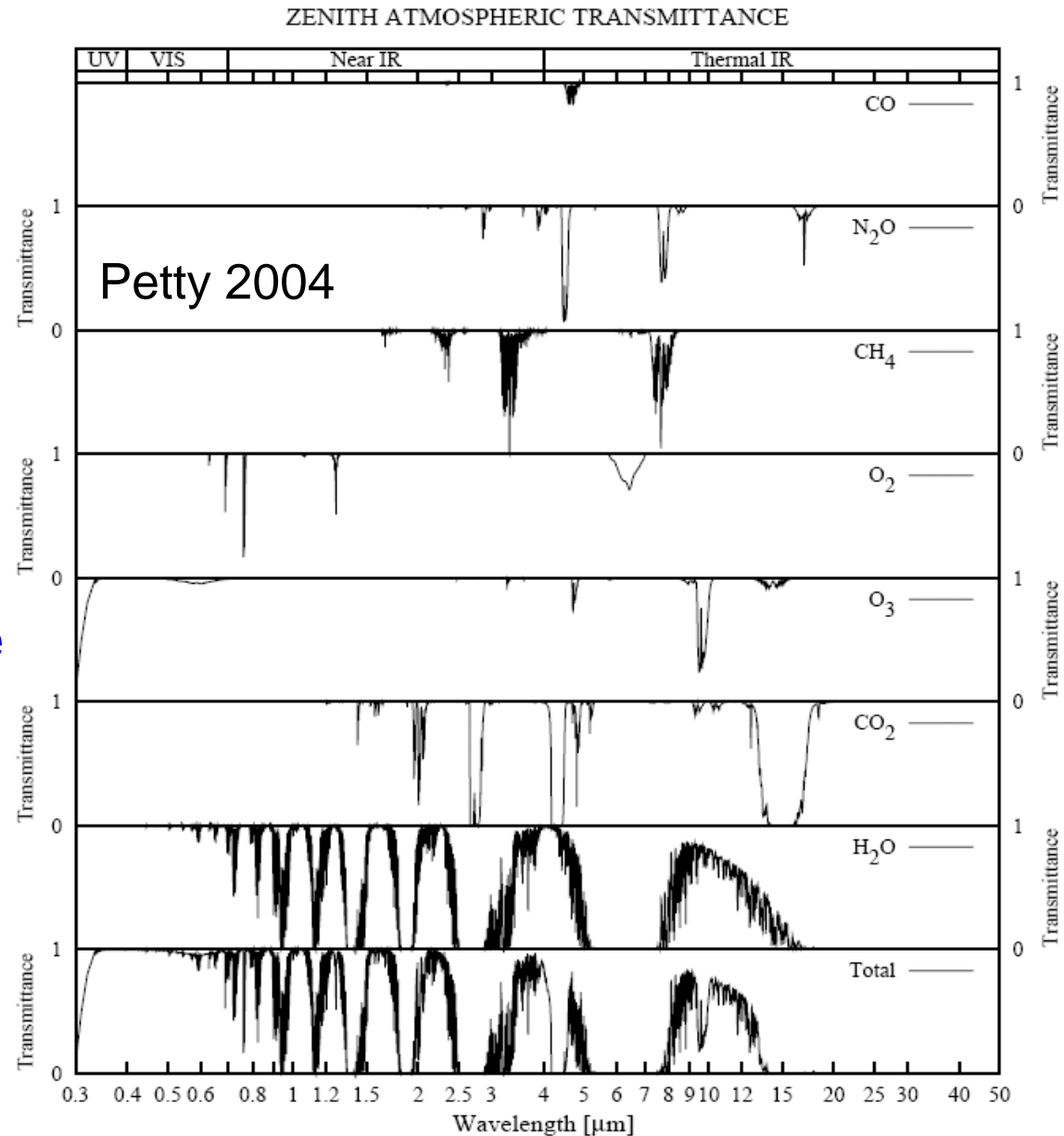
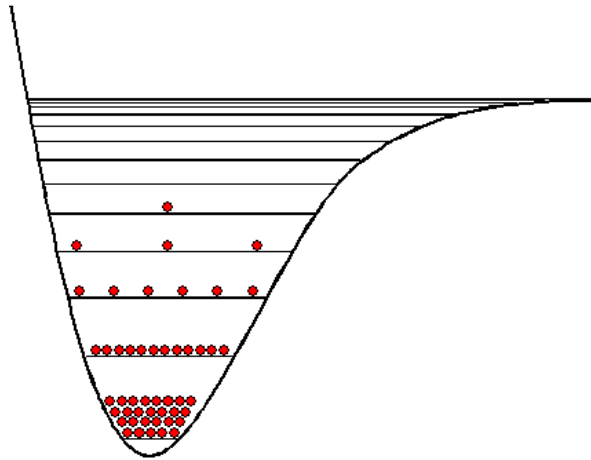# The Boltzmann Distribution

$$N(E_i) \approx N_i \exp(-E_i / kT)$$

- For a molecule to be excited from a lower state, it must be in the lower state to start with!
- In thermodynamic equilibrium, the number of molecules in a given state is determined by the Boltzmann Distribution
- Under atmospheric conditions (below ≈80 km), collisions determine how many molecules are in which state.
- They maintain the Boltzmann distribution, a state called "local thermodynamic equilibrium"

Profoundly important! It explains

(1) why the Planck Function can be used to determine atmospheric emission

(2) how the loss or gain of radiative energy by the (radiatively active) molecules is thermalised and shared by all molecules

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Radiative transfer calculations

To calculate the irradiances and heating rates for any particular atmospheric profiles, we need various inputs

vertical profile of radiatively active gases (H_2O, O_3, CO_2 ...) and temperature

database of spectroscopic properties of molecules (e.g. HITRAN, GEISA)

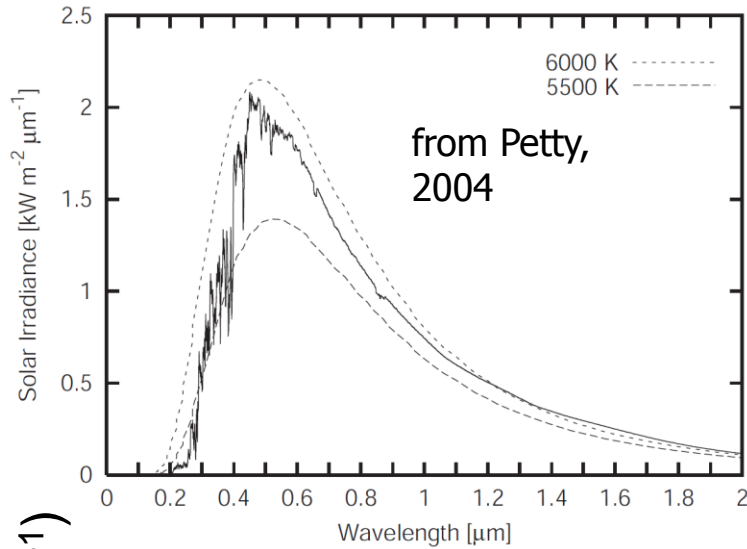profiles of (and optical properties of) clouds and aerosols

solar spectrum, solar zenith angle ...

radiative transfer code – numerical solution of the radiative transfer equations and technique for calculating transmittances.

spectral and wavelength integrated irradiances and heating rates

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Real (non-black-body) spectra

Solar

Thermal IR

from Petty, 2004

Arctic
(a) 20 km looking down

Petty 2004
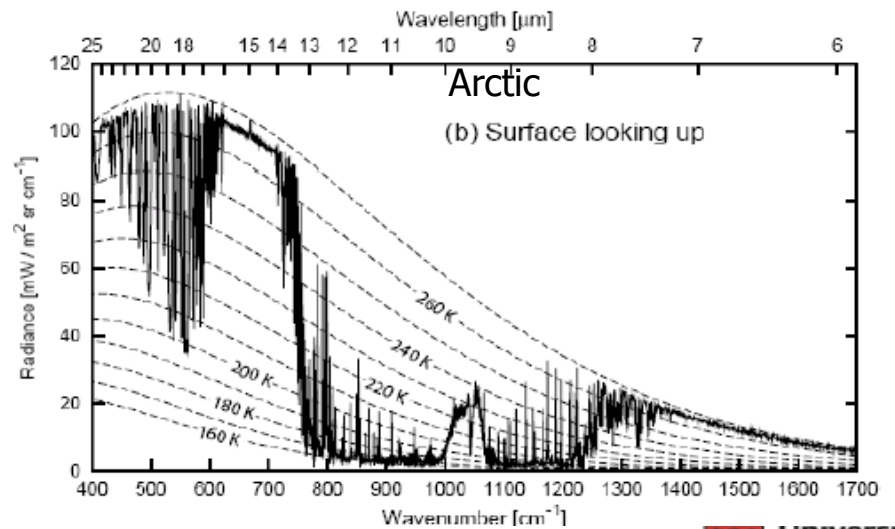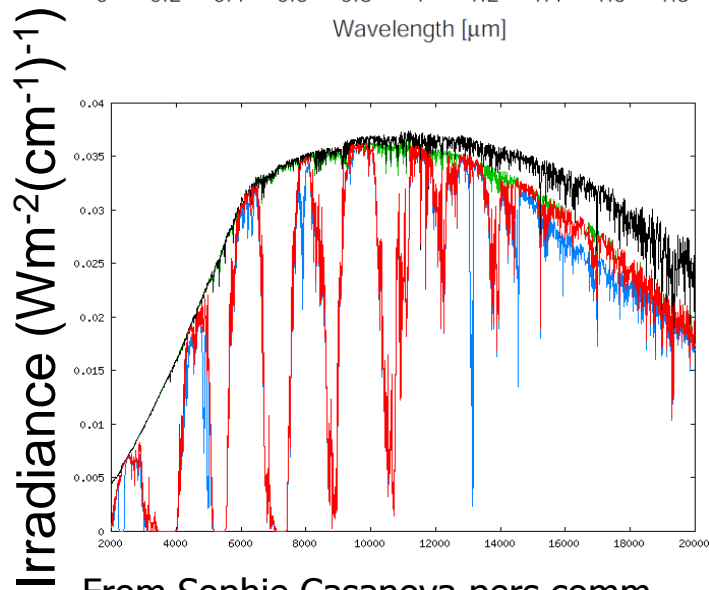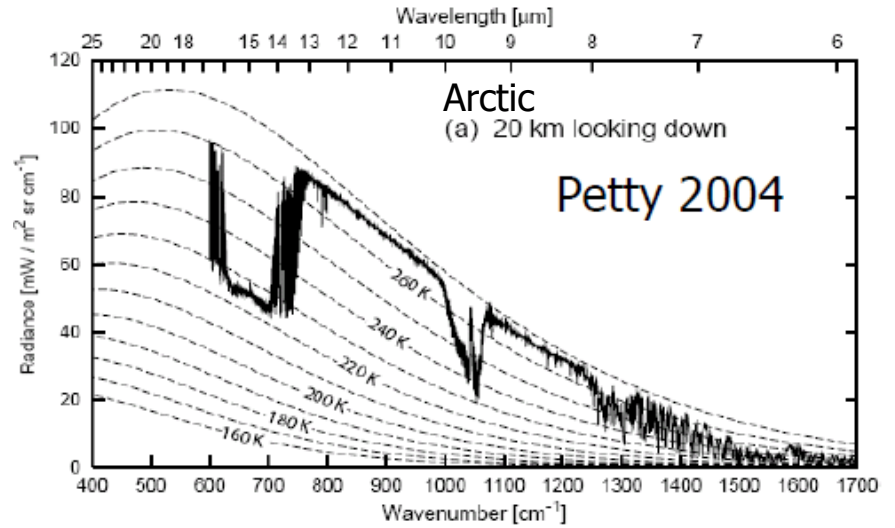
From Sophie Casanova pers.comm.

Arctic
(b) Surface looking up

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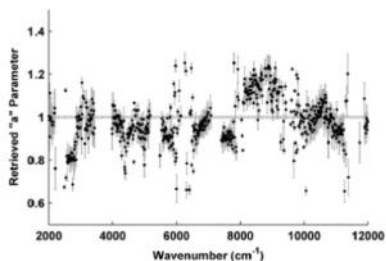
IF. YEAR.THEN. NEW HITRAN VERSION

The HITRAN2012 molecular spectroscopic database

L.S. Rothman [a,*], I.E. Gordon [a], Y. Babikov [b], A. Barbe [c], D. Chris Benner [d], P.F. Bernath [e], M. Birk [f], L. Bizzocchi [g], V. Boudon [h], L.R. Brown [i], A. Campargue [j], K. Chance [a], E.A. Cohen [i], L.H. Coudert [k], V.M. Devi [d], B.J. Drouin [i], A. Fayt [l], J.-M. Flaud [k], R.R. Gamache [m], J.J. Harrison [n], J.-M. Hartmann [k], C. Hill [o], J.T. Hodges [p], D. Jacquemart [q], A. Jolly [k], J. Lamouroux [k,m], R.J. Le Roy [r], G. Li [a], D.A. Long [p], O.M. Lyulin [b], C.J. Mackie [a,1], S.T. Massie [s], S. Mikhailenko [b], H.S.P. Müller [t], O.V. Naumenko [b], A.V. Nikitin [b], J. Orphal [u], V. Perevalov [b], A. Perrin [k], E.R. Polovtseva [b], C. Richard [a], M.A.H. Smith [v], E. Starikova [b], K. Sung [i], S. Tashkun [b], J. Tennyson [o], G.C. Toon [i], Vl.G. Tyuterev [c], G. Wagner [f]

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The updating process

Fig. 5. Schematic overview of the ozone ¹⁶O₃ transitions in the HITRAN2012 edition. Each of the 263,886 lines corresponds to a circle or a triangle on the log intensity scale. New data added since the 2008 edition are marked with red full circles. (To understand the use of color in this figure, please see the web version of this paper.)

Includes both new measurements and theoretical analyses
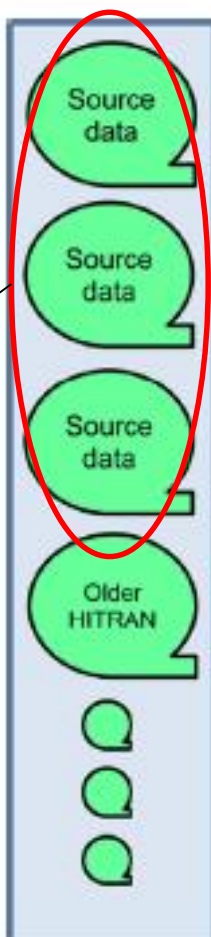
Basic rules:
- reasonable bounds for parameters
- selection rules obeyed; no duplicated transitions
- no coalesced multiplets
- zero point energy correct
- standards and units OK– 296K, isotopic abundance correct
- consistent partition sum
- consistency of quantum notation, uncertainties, and references
- correct format of parameters obeyed

Errors & Outliers: Compare to previous line lists; plot

Comparisons with observations: Examine residuals from simulation of atmospheric high-resolution observations, or independent raw laboratory measurements
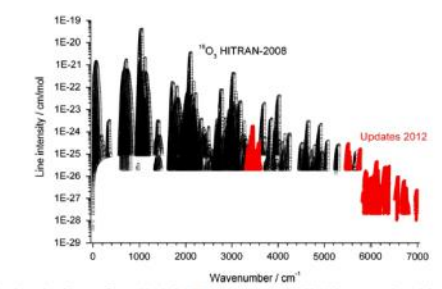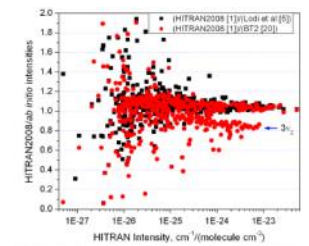
HITRAN committee: Final evaluation by committee members

Fig. 3. Comparison of HITRAN2008 with the values of BT2 [20] (red circles) and with the values of Lodi et al. [5] (black squares) in the 4700–5000 cm⁻¹ region.

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Line positions, intensities and widths are vital

Table 1
Description of the quantities present in the 160-character records (transitions) of the line-by-line portion of the HITRAN database.

Parameter	Meaning	Field length	Type	Comments or units
M	Molecule number	2	Integer	HITRAN chronological assignment
I	Isotopologue number	1	Integer	Ordering by terrestrial abundance
ν	Vacuum wavenumber	12	Real[a]	cm^{-1}
S	Intensity	10	Real[a]	$cm^{-1}/(molecule\ cm^{-2})$ at standard 296 K
A	Einstein-A coefficient	10	Real	s^{-1}
γ_{air}	Air-broadened half width	5	Real	HWHM at 296 K (in $cm^{-1}\ atm^{-1}$)
γ_{self}	Self-broadened half width	5	Real	HWHM at 296 K (in $cm^{-1}\ atm^{-1}$)
E''	Lower-state energy	10	Real	cm^{-1}
n	Temperature-dependence coefficient	4	Real	Temperature-dependent exponent for γ_{air}
δ	Air pressure-induced line shift	8	Real	$cm^{-1}\ atm^{-1}$ at 296 K
V'	Upper-state "global" quanta	15	Character	See Table 3 in Ref. [2]
V''	Lower-state "global" quanta	15	Character	See Table 3 in Ref. [2]
Q'	Upper-state "local" quanta	15	Character	See Table 4 in Ref. [2]
Q''	Lower-state "local" quanta	15	Character	See Table 4 in Ref. [2]
Ierr	Uncertainty indices	6	Integer	Accuracy for 6 critical parameters (ν, S, γ_{air}, γ_{self}, n, δ), see Table 5 of Ref. [2]
Iref	Reference indices	12	Integer	References for 6 critical parameters (ν, S, γ_{air}, γ_{self}, n, δ)
*	Flag	1	Character	Pointer to program and data for the case of line mixing
g'	Statistical weight of upper state	7	Real	See details in Ref. [3]
g''	Statistical weight of lower state	7	Real	See details in Ref. [3]

[a] Double precision is recommended for these parameters in order to preserve significant digits and to accommodate some intensity values with very low exponents.

# 47 species with line data available plus more with cross-section data

Table 2
Molecules and isotopologues represented in the line-by-line portion of HITRAN.

Molecule	Isotopologue[a]	HITRAN2012 spectral coverage (cm^{-1})	HITRAN2008 spectral coverage (cm^{-1})	HITRAN2012 number of transitions	HITRAN2008 number of transitions
(1) H_2O	161	0–25,711	0–25,233	142,045	37,432
	181	0–19,918	0–14,519	39,903	9753
	171	0–19,946	10–14,473	27,544	6992
	162	0–22,708	0–22,708	13,237	13,238
	182	0–3825	0–3825	1611	1611
	172	1234–1599	1234–1599	175	175
(2) CO_2	626	345–12,785	352–12,785	169,292	128,170
	636	406–12,463	438–12,463	70,611	49,777
	628	0–9558	0–11,423	116,482	79,958
	627	0–9600	0–8271	72,525	19,264
	638	489–6745	489–6745	26,737	26,737
	637	583–6769	583–6769	2953	2953
	828	491–8161	491–8161	7118	7118
	827	626–5047	626–5047	821	821
	727[b]	535–6933	c	5187	c
	838[b]	4599–4888	4599–4888	121	121
(3) O_3	666	0–6997	0–5787	261,886	249,456
	668	0–2768	0–2768	44,302	44,302
	686	1–2740	1–2740	18,887	18,887
	667	0–2122	0–2122	65,106	65,106
	676	0–2101	0–2101	31,935	31,935
(4) N_2O	446	0–7797	0–7797	33,074	33,074
	456	5–5086	5–5086	4222	4222
	546	4–4704	4–4704	4592	4592
	448	542–4672	542–4672	4250	4250
	447	550–4430	550–4430	1705	1705
(5) CO	26	3–8465	3–8465	1019	917
	36	3–6279	3–6279	797	780
	28	3–6267	3–6267	770	760
	27	3–6339	3–6339	728	728
	38	3–6124	3–6124	712	712
	37	1807–6197	1807–6197	580	580
(6) CH_4	211	0–11,502	0–9200	336,830	212,061
	311	0–11,319	0–6070	72,420	28,793
	212	7–6511	7–6511	54,550	45,024
	312	959–1695	959–1695	4213	4213

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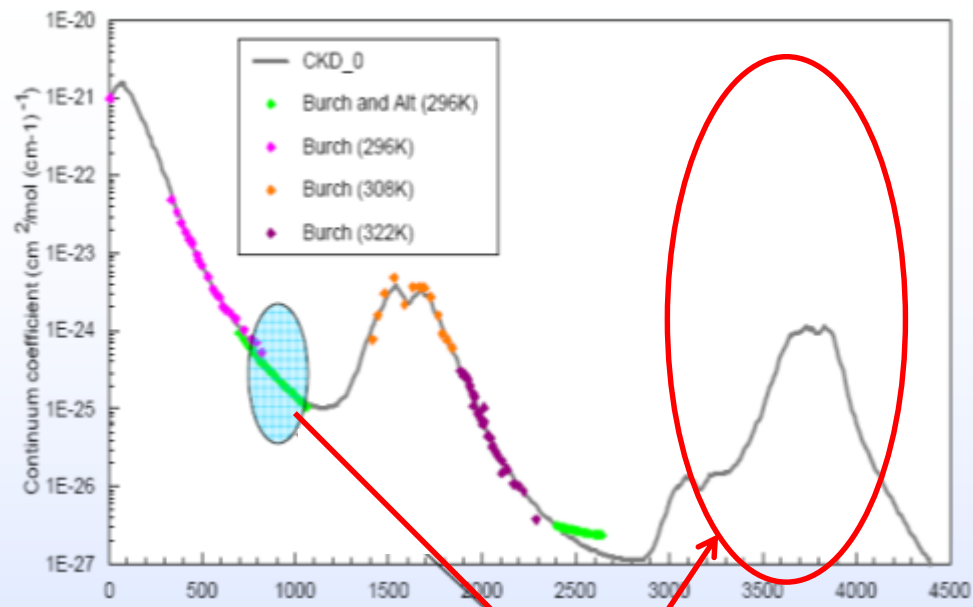
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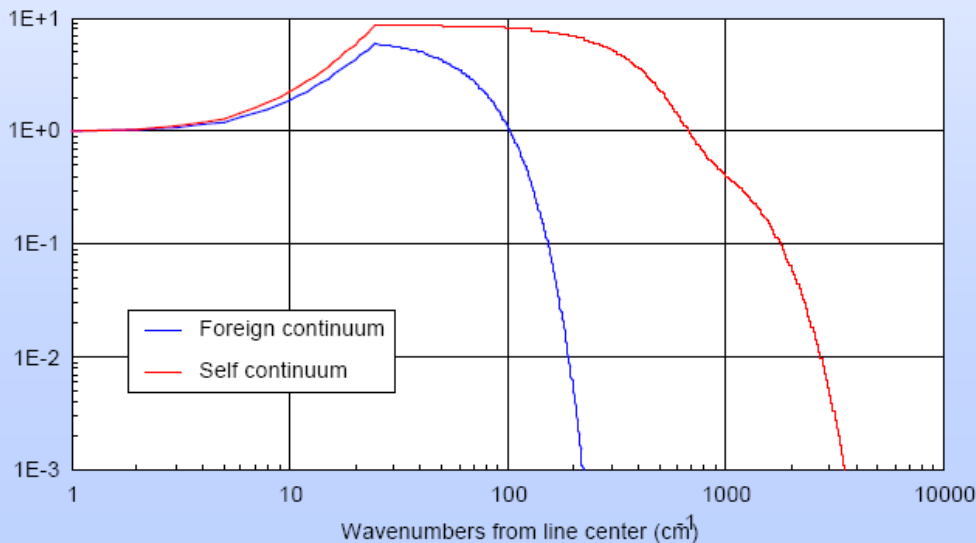# Between the water bands ... the water vapour continuum
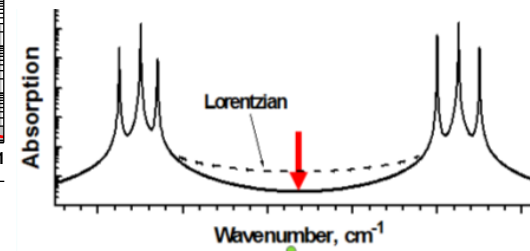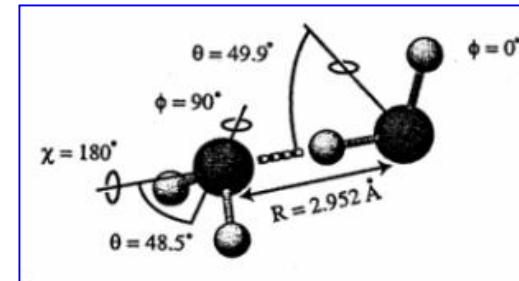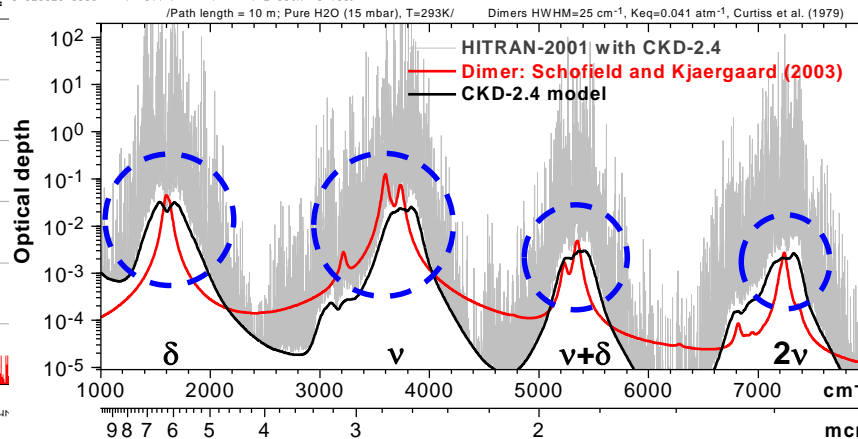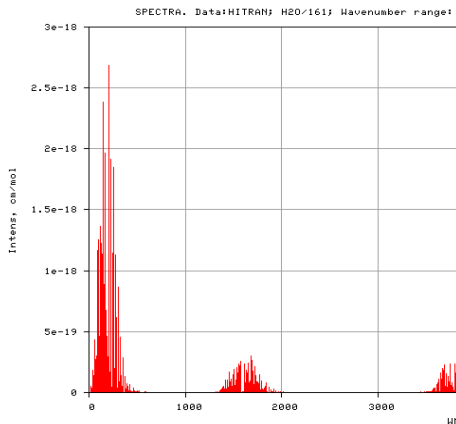
- Leading importance in the 10 micron mid-infrared window, but also important between the other water vapour bands

- Not settled scientific cause – could be a mix of far-wings of water vapour lines, collision-induced absorption and/or due to water vapour dimers

- But more importantly its strength in the near-IR windows is uncertain. That is what will concern us here

The CKD (Clough-Kneizys-Davies) continuum model

- A *major* step forward in the representation of continuum (rtweb.aer.com) – used in most radiative transfer schemes for models and satellite retrievals

- Based on *empirical* modification of the line shapes in "data rich" spectral regions to force agreement with continuum observations: this modified line shape is then used at all wavelengths

- Continually updated since 1980s … latest version is (Mlawer-Tobin) MT-CKD_2.5 with a somewhat different formulation

- Semi-empirical formulation means that it does <u>not</u> *explain* the continuum

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Original CKD model

Self continuum

$$f(\nu - \nu_0) = \frac{1}{\pi} \frac{\alpha}{(\nu - \nu_0)^2 + \alpha^2} \chi(\nu - \nu_0)$$

χ-functions: CKD continuum formulation

- Foreign continuum
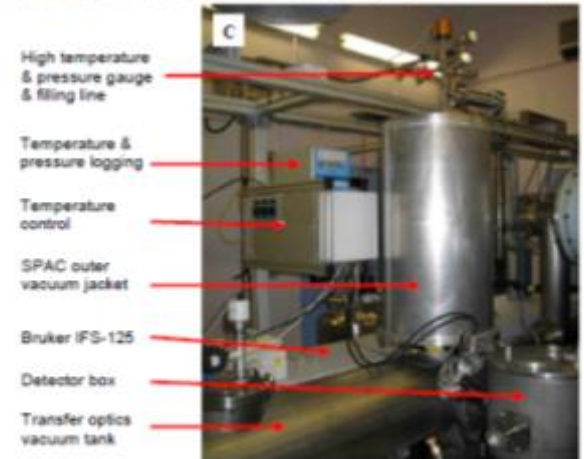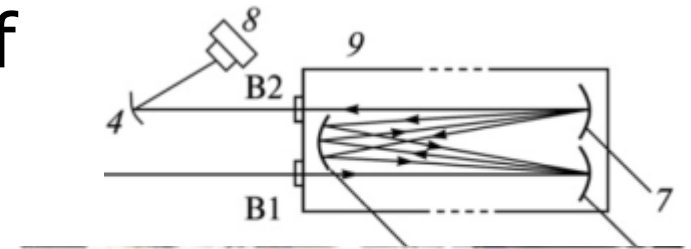- Self continuum

Wavenumbers from line center (cm⁻¹)

- Limited spectral regions to fit the model to observations
- Therefore, continuum in many spectral regions lack experimental support

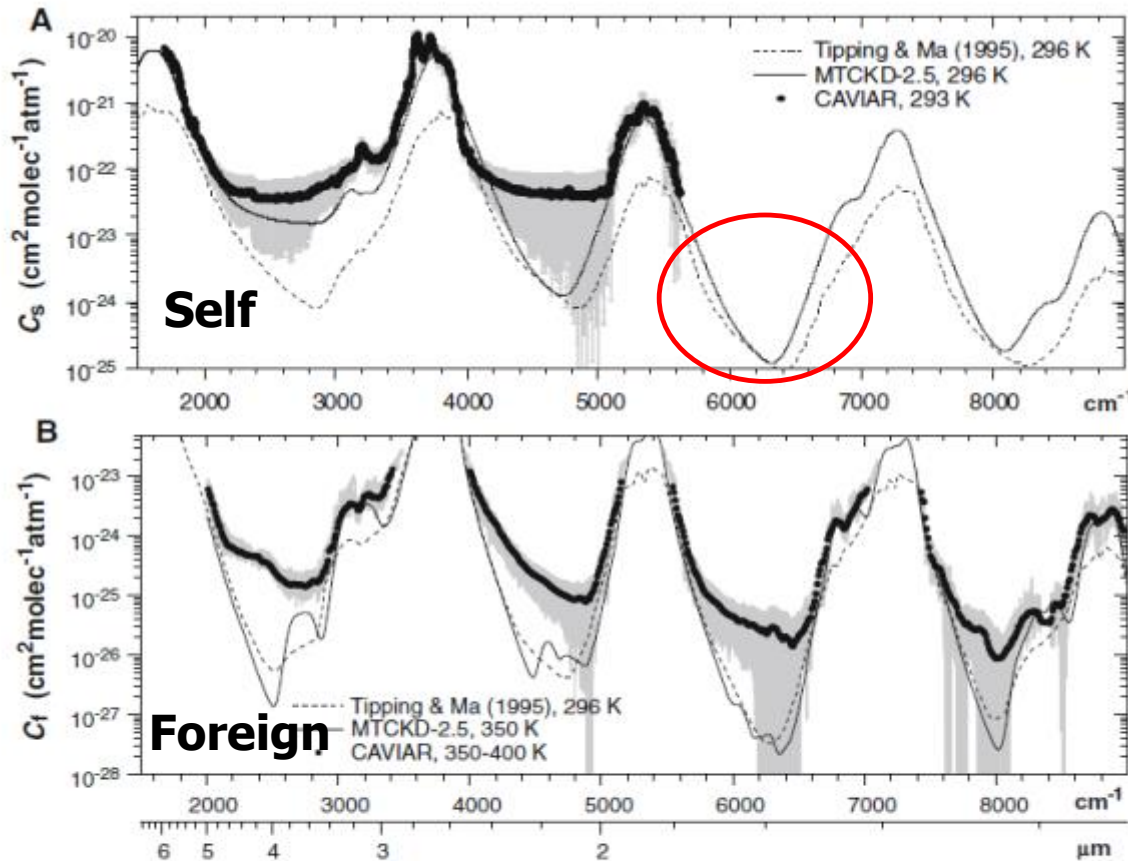See Mlawer et al. (Phil Trans Roy Soc A, 2012)

Beyond CKD …

- To *characterise the continuum* over broad spectral regions and broad range of conditions in both lab and field

- To *explain the continuum* via advances in understanding of water spectroscopy

- *CAVIAR … **C**ontinuum **A**bsorption in the **Visible** and **I**nfrared and its **A**tmospheric **R**elevance* … multi-institute consortium led from Reading from 2006-2011

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- Continuum absorption, especially in near-IR, is very weak over "lab distances"

- Hence we need a combination of high vapour pressures and long-path lengths

- Water vapour condenses too easily! To get high vapour pressures we must observe at high temperatures

- But conditions are then not "atmospheric" – need to extrapolate to atmospheric conditions

Experimental Challenges

High temperature & pressure gauge & filling line

Temperature & pressure logging

Temperature control

SPAC outer vacuum jacket

Bruker IFS-125

Detector box

Transfer optics vacuum tank

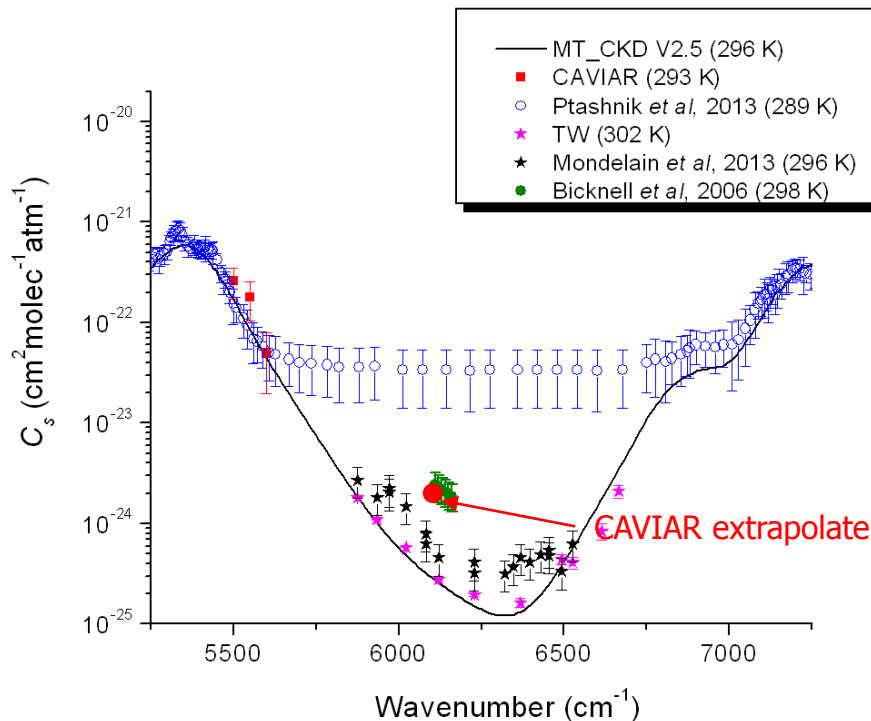# Summary of CAVIAR near-infrared continuum measurements

Fig. 3 Self- and foreign-continuum cross-section (*upper and lower panels* respectively) as retrieved from laboratory measurements in Ptashnik et al. (2011b, 2012) (CAVIAR), along with their associated uncertainties, compared to the far-wing model of Tipping and Ma (1995) and the MTCKD-2.5 continuum model

(MT)-CKD self continuum *appears* incorrect by typically an order of magnitude in some near-IR windows

But there is considerable controversy/uncertainty especially in the 1.6μm window ...

(Shine et al 2012, Surveys in Geophysics)

Continuum strength

Temperature dependence of the water vapor self-continuum by cavity ring-down spectroscopy in the 1.6 μm transparency window

D. Mondelain[1,2], S. Manigand[1,2], S. Kassi[1,2], and A. Campargue[1,2]

Legend:
- MT_CKD V2.5 (296 K)
- CAVIAR (293 K)
- Ptashnik et al, 2013 (289 K)
- TW (302 K)
- Mondelain et al, 2013 (296 K)
- Bicknell et al, 2006 (298 K)

CAVIAR extrapolate

Mondelain et al. (JGR 2014)

Different laboratory techniques lead to dramatically different characterizations of continuum strength in this window

Is one right? Is one better suited for understanding *atmospheric* absorption?

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Temperature dependence

Temperature dependence of the water vapor self-continuum by cavity ring-down spectroscopy in the 1.6 μm transparency window
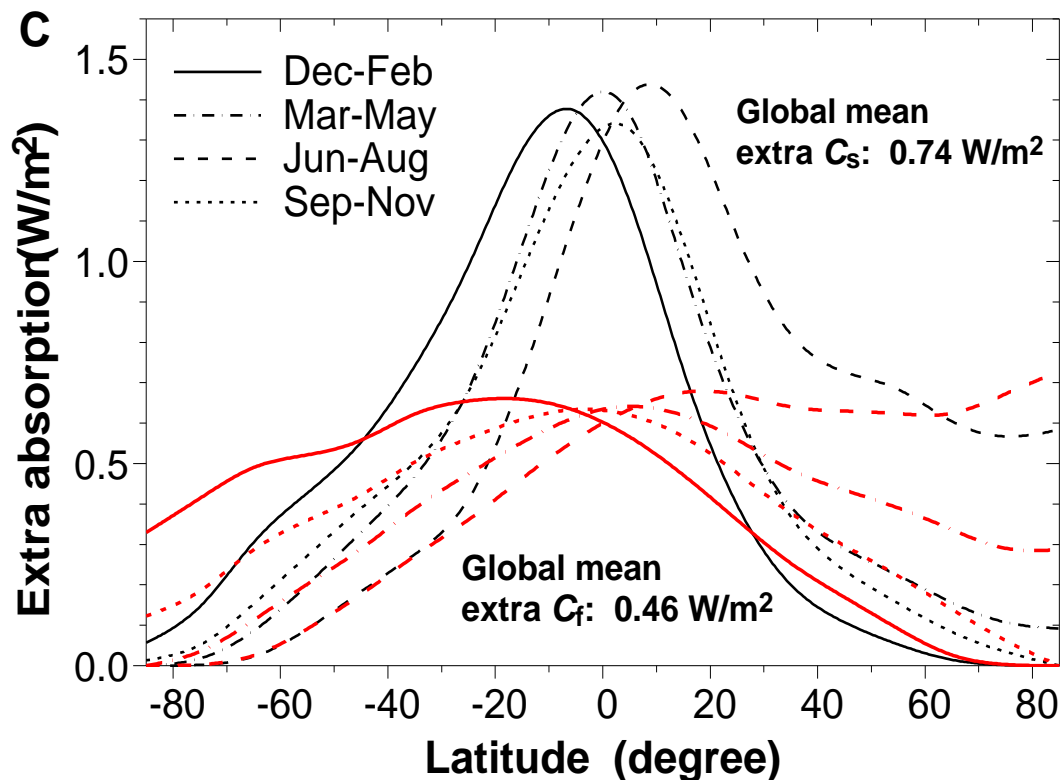
D. Mondelain[1,2], S. Manigand[1,2], S. Kassi[1,2], and A. Campargue[1,2]
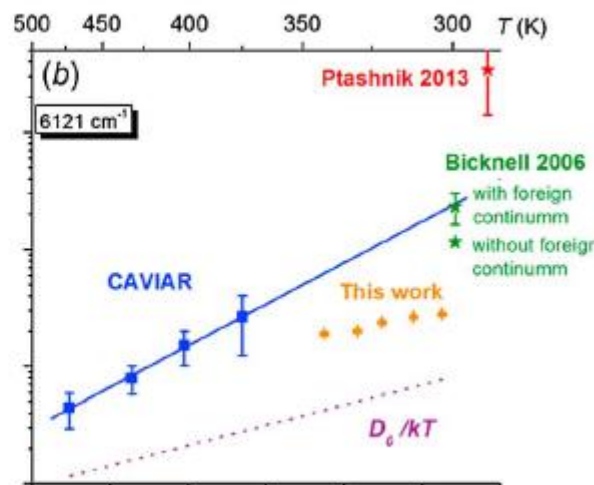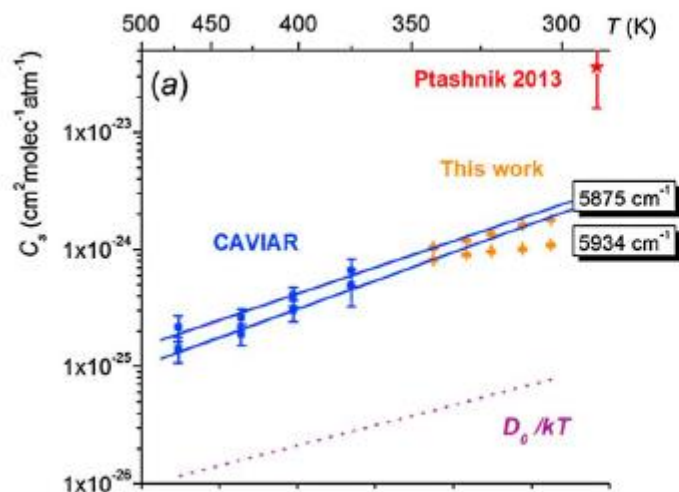
Towards the edge of window, CAVIAR and CRDS are consistent with an assumed temperature dependence

But near the centre of the window this is not the case - surprisingly little temperature dependence in CRDS

Mondelain et al. (JGR 2014)

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Global impact of new continuum for clear skies

New continuum increases the global-mean clear-sky atmospheric shortwave absorption by 2% compared to CKD. Would be even more, if the 1.6 μm band is as strong as shown in some measurements

In a warming world, this absorption increases by 12% more using CAVIAR continuum

Ptashnik et al. (Phil Trans Roy Soc, 2012)

Rädel et al. (QJRMS, 2015)

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Impact on remote sensing of cloud properties

Satellite retrievals of cloud droplet radius (and much else) use 4900 cm^{-1} window (amongst others)

If new continuum is used, it could systematically reduce the retrieved droplet radius by typically about 1 μm (in 10 μm). Depends on cloud height and location
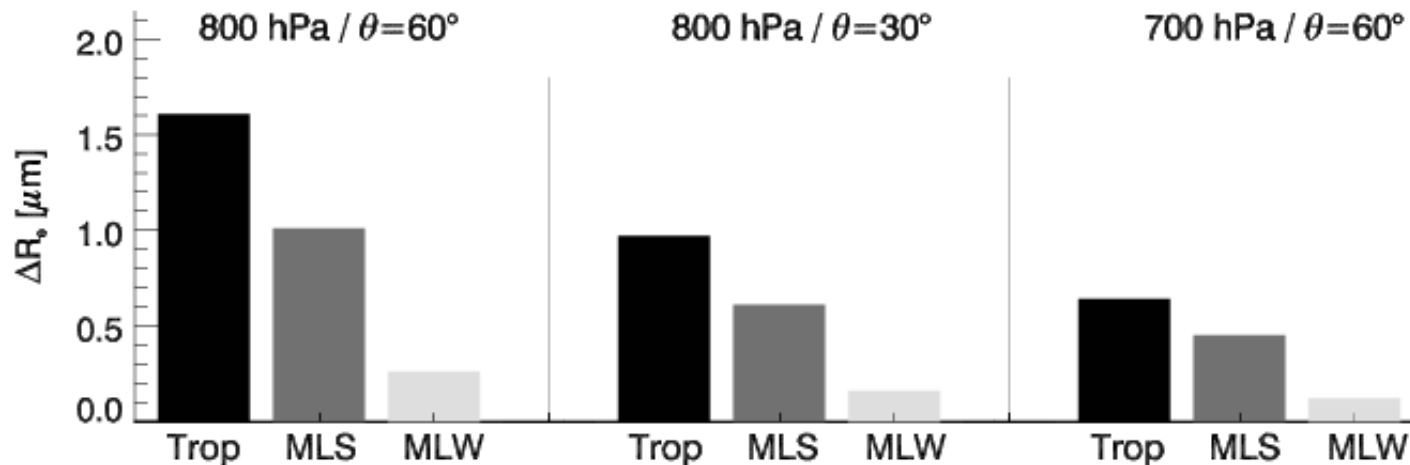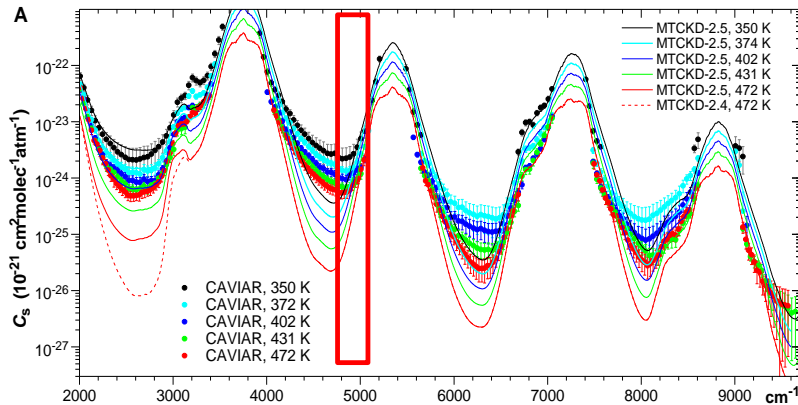
Shine et al., Surveys in Geophys, 2012

Where next at 1.6 μm?

- Analysis of sun-pointing FTS measurements made during CAVIAR (NERC student with NPL)

- Coupling RAL spectrometer to a new "super-continuum light source" – to increase path and signal-to-noise

- Need for a tight intercomparison of laboratory techniques for measuring continuum

- Is there subsidiary evidence (e.g. remote sensed versus in situ data) ?
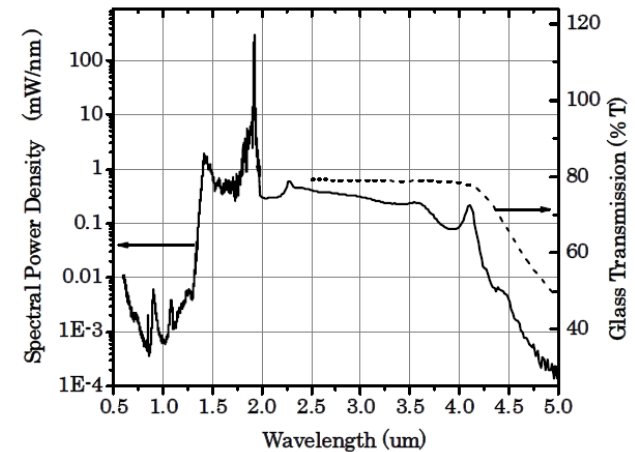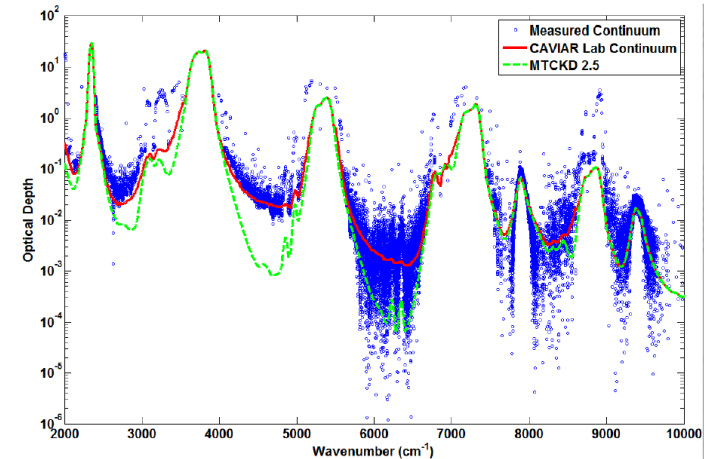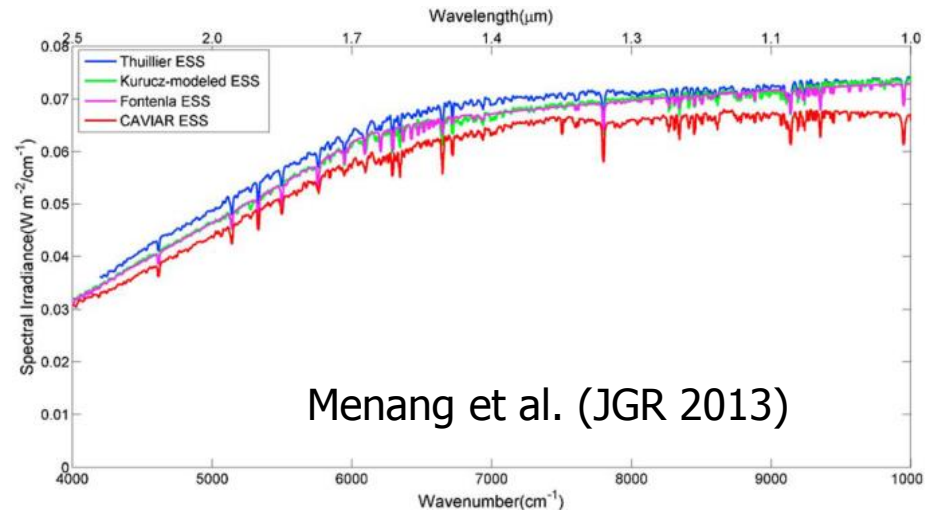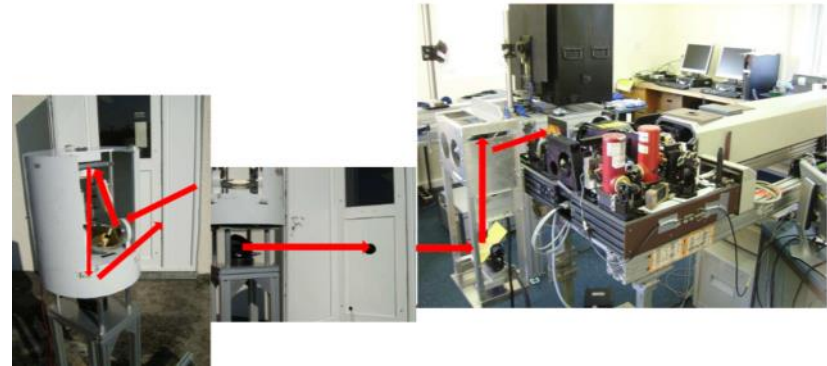

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Contents

- Incoming solar radiation
- A brief introduction to molecular spectroscopy and the HITRAN database
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Incoming top-of-atmosphere solar radiation in the solar near-infrared

- A quite surprising and little known controversy on a rather "basic" number

- How much solar radiation (and what is its spectral distribution) is there in the solar-near infrared?

- Our analysis of ground-based observations indicated existing solar spectra may be wrong by 7-8% (i.e. we have "lost" about 30 W m^{-2} of total solar irradiance ☹)
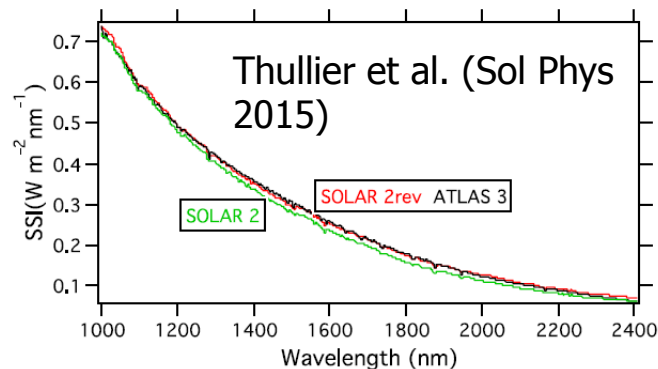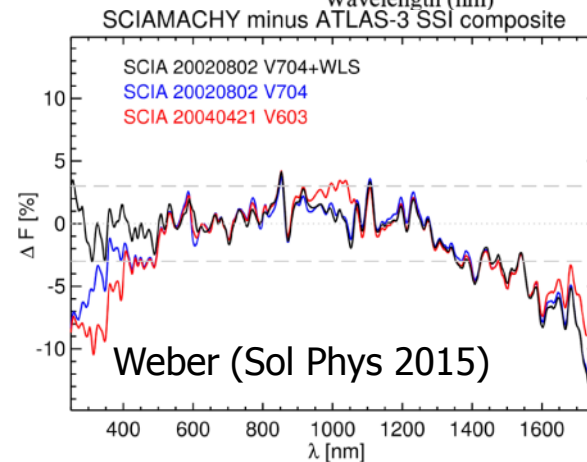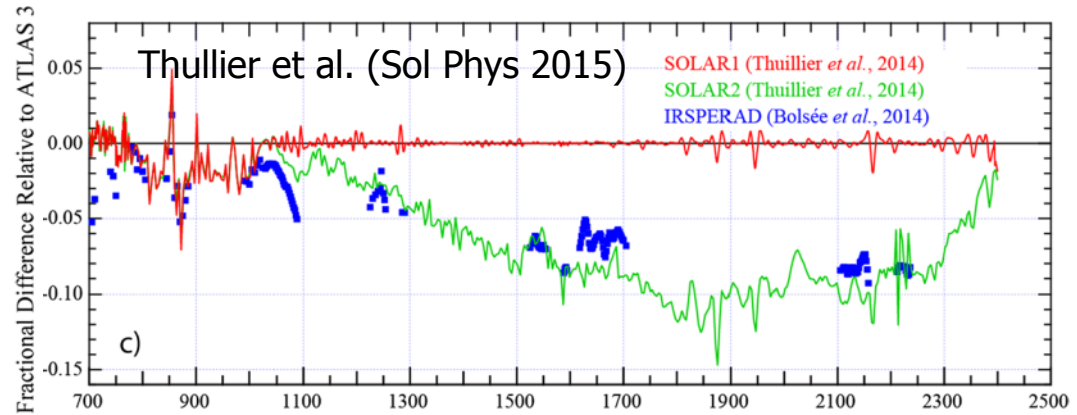
NPL FTS and sun-tracker

Menang et al. (JGR 2013)

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Subsequent studies ...

- Subsequent support from other both ground-based and satellite-based analyses

- But has led to real uncertainty about the calibration of the space-based instrument

- A lack of closure – most recently a revised calibration of some space-based data has removed the discrepancy but this remains contentious!

Thullier et al. (Sol Phys 2015)

SOLAR1 (Thuillier *et al.*, 2014)
SOLAR2 (Thuillier *et al.*, 2014)
IRSPERAD (Bolsée *et al.*, 2014)

SCIAMACHY minus ATLAS-3 SSI composite

SCIA 20020802 V704+WLS
SCIA 20020802 V704
SCIA 20040421 V603

Weber (Sol Phys 2015)

Thullier et al. (Sol Phys 2015)

SOLAR 2rev   ATLAS 3

SOLAR 2

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