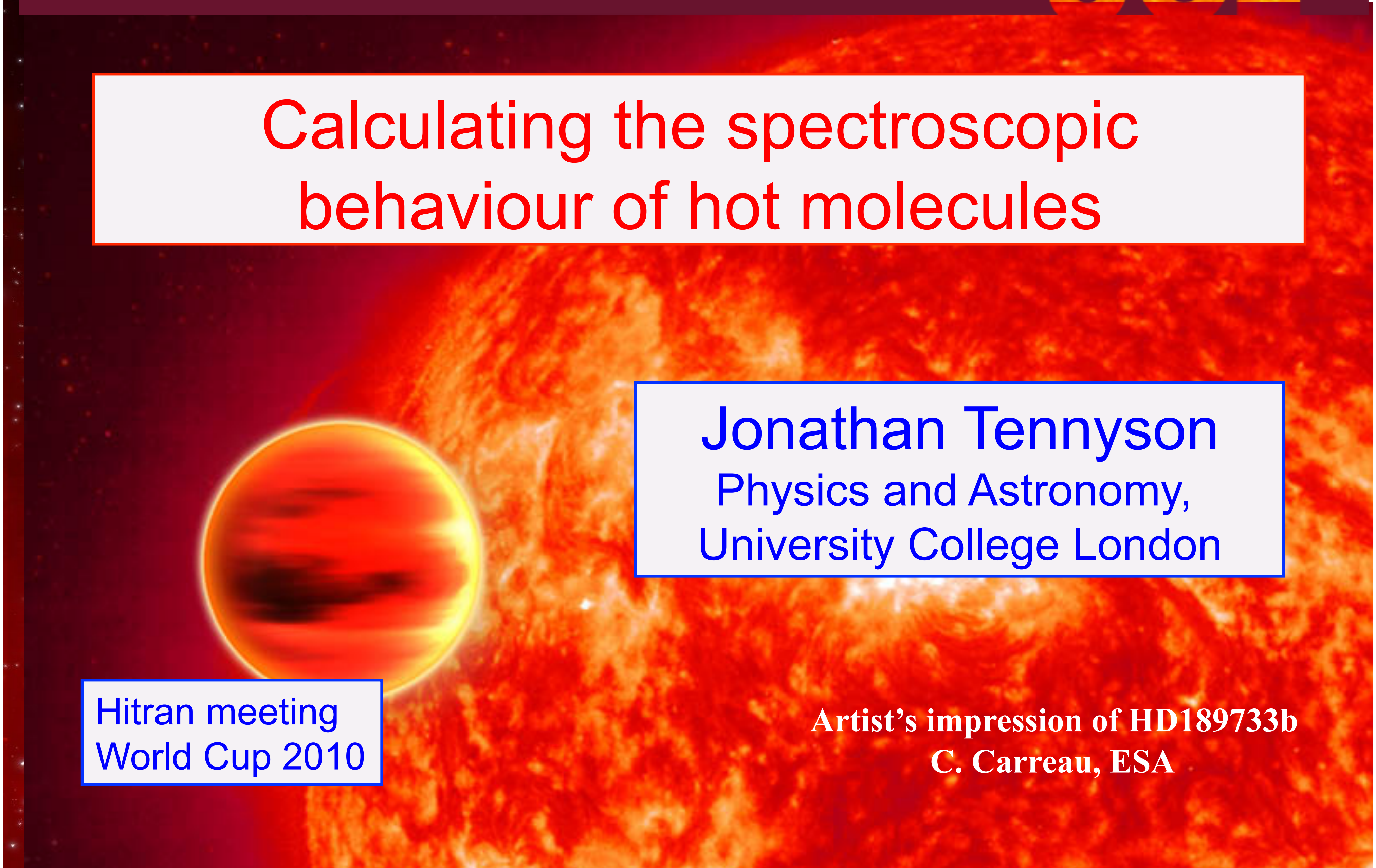
# Calculating the spectroscopic behaviour of hot molecules

Jonathan Tennyson
Physics and Astronomy,
University College London

Hitran meeting
World Cup 2010



Artist's impression of HD189733b
C. Carreau, ESA

# Spectroscopy at T >500 K

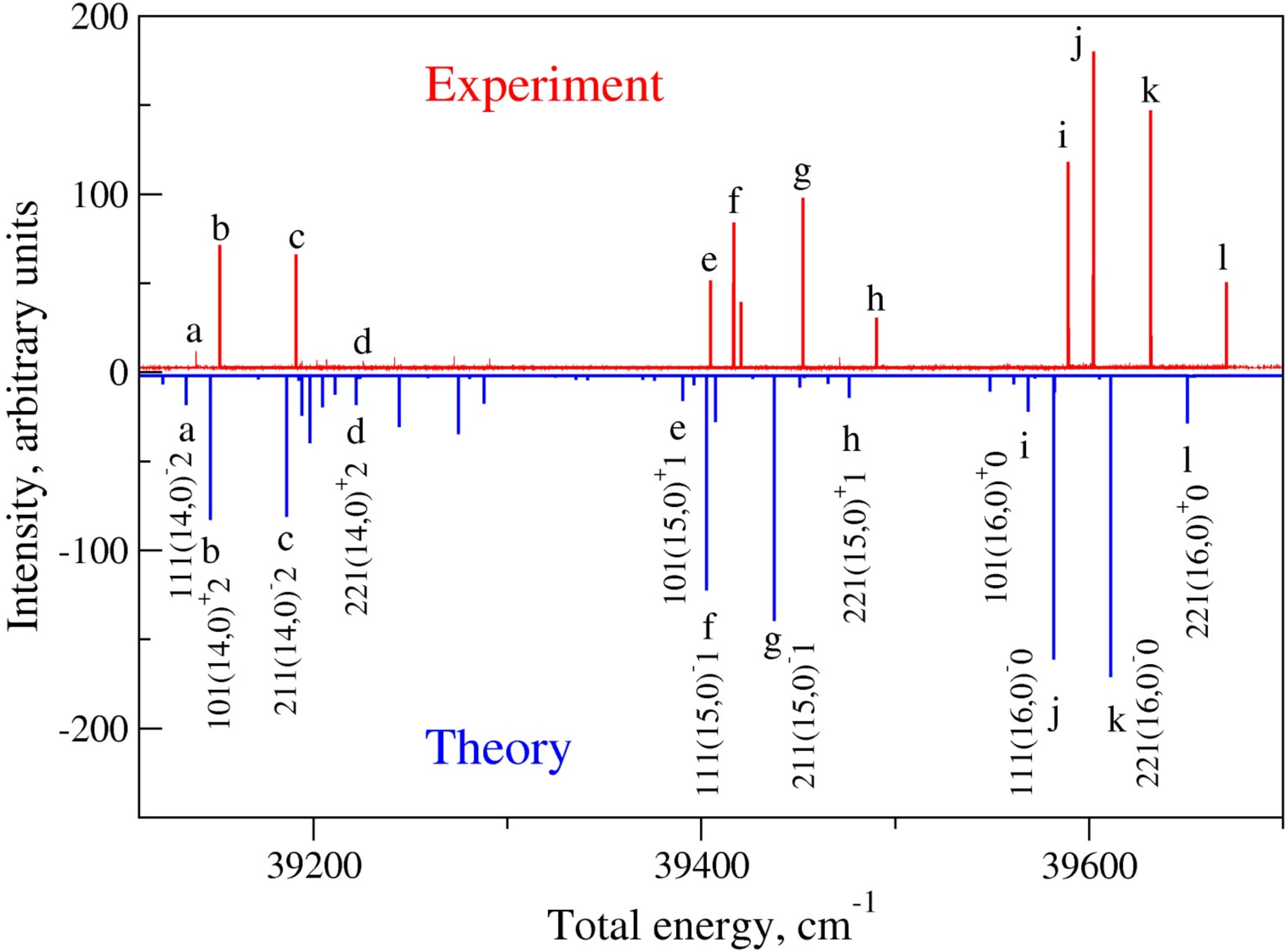
- Flames (+exhaust gases)
- Cool stars
- Brown dwarfs
- Extrasolar planets
- Non-LTE problems

**New edition of HITEMP**:

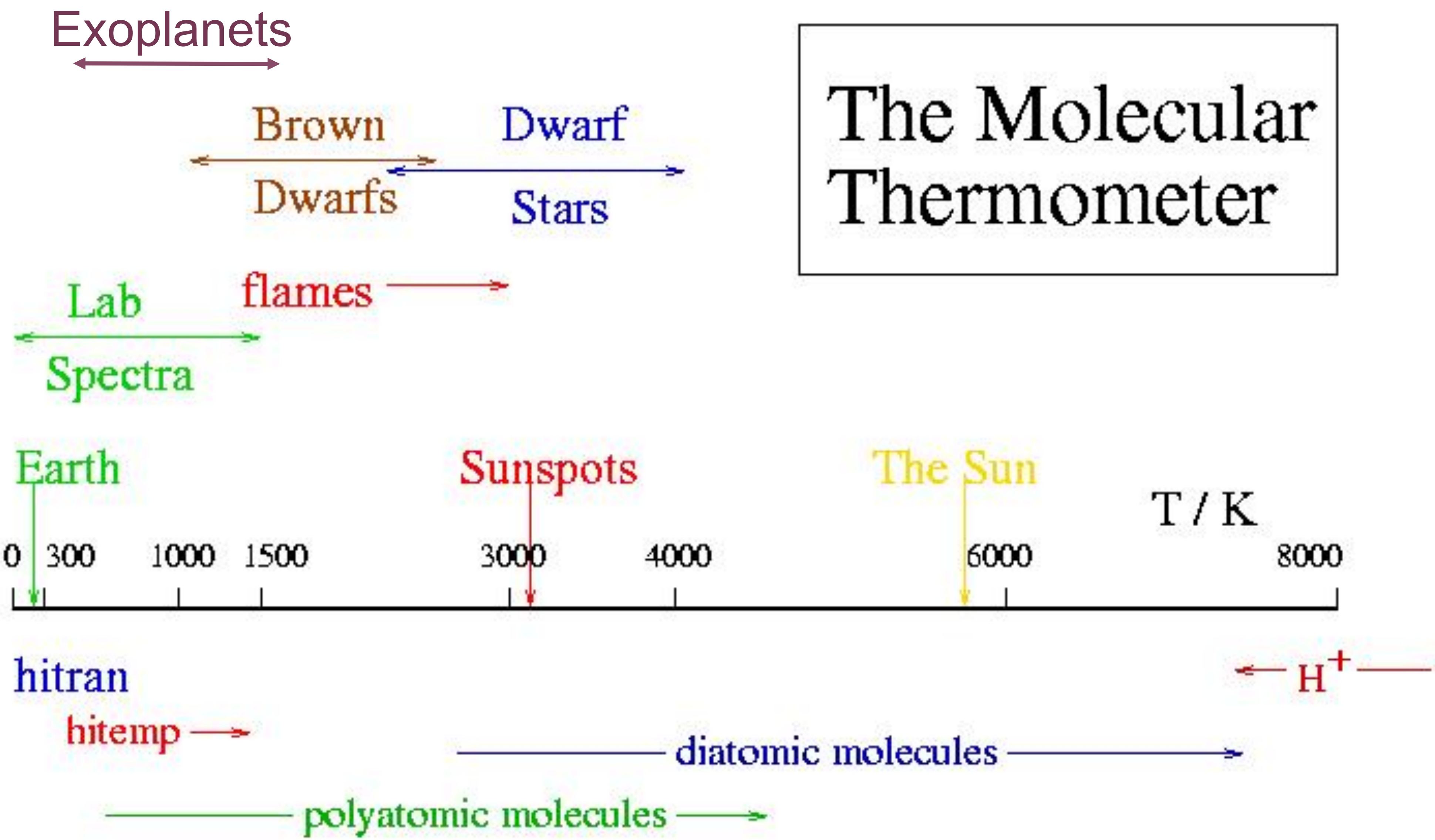
Molecules contained: $H_2O$, $CO_2$, NO, OH, CO

LS Rothman, IE Gordon, RJ Barber, H Dothe, RR Gamache, A Goldman, VI Perevalov, SA Tashkun + J Tennyson, JQSRT (in press)

# Water @ Dissociation: 3-photon spectroscopy




M. Grechko et al, State-selective spectroscopy of water up to its first dissociation limit,, J. Chem. Phys., 131, 221105 (2009).


Exoplanets
Brown Dwarfs
Dwarf Stars
The Molecular Thermometer
Lab Spectra
flames
Earth
Sunspots
The Sun
T / K
0
300
1000
1500
3000
4000
6000
8000
hitran
hitemp
$H^+$
diatomic molecules
polyatomic molecules

# Opacity of cool stars, brown dwarfs & exoplanets

- Closed shell diatomics: $H_2$, CO, etc
- Transition metal diatomics: TiO, FeH, etc
- Triatomic molecules: $H_2O$, HCN, $C_3$ etc ($CO_2$, $O_3$)
- Tetratomic molecule: $NH_3$, HCCH
- Pentatomic: $CH_4$
- Hydrocarbons: $C_2H_4$, $C_2H_6$, others?
- Dust (other biomarkers eg $HNO_3$?)

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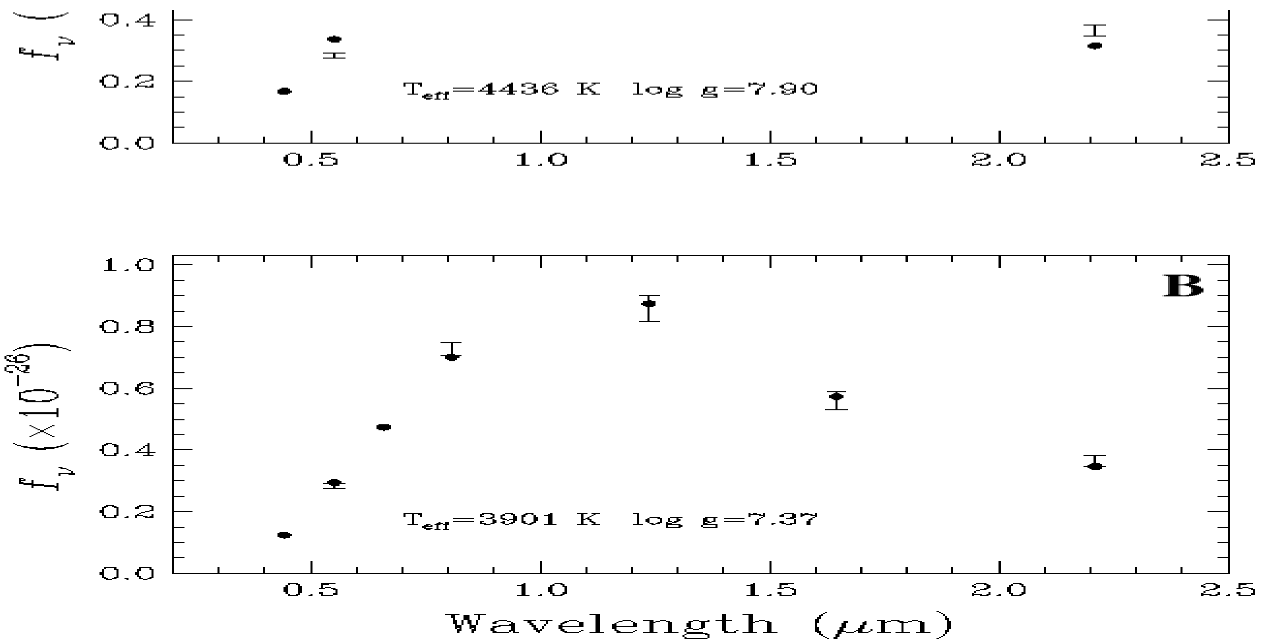
# Modeling spectra @ 1000 -3000 K

- Spectra very dense – cannot get T from black-body fit.
- Synthetic spectra require huge databases
  > $10^6$ vibration-rotation transitions per triatomic molecule
- Sophisticated opacity sampling techniques.
- Partition functions also important

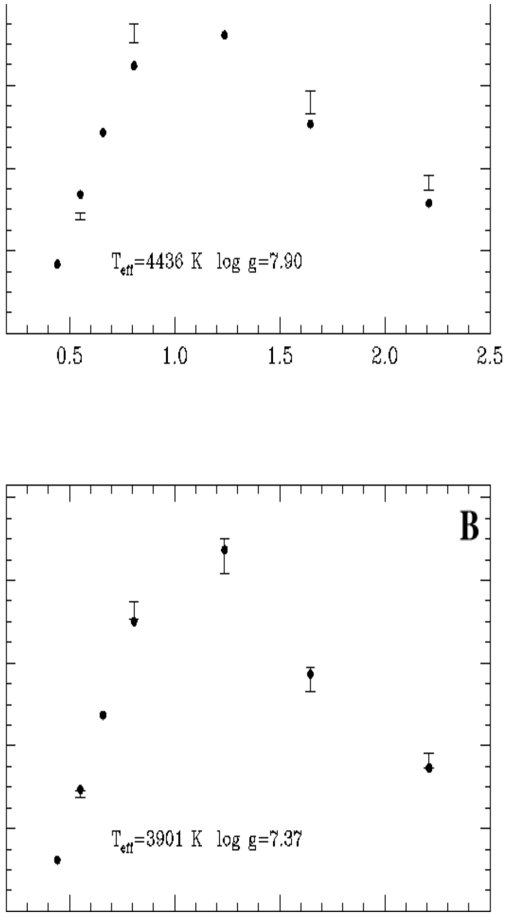
## Partition functions are important




Model of cool, metal-free magnetic white dwarf WD1247+550 by Pierre Bergeron (Montreal)

Is the partition function of $H_3^+$ correct?

# Partition functions are important




Model of WD1247+550 using ab initio $H_3^+$ partition function of Neale & Tennyson (1996)

## *Calculated $H_3^+$ linelist of Neale, Miller and Tennyson (1993) used extensively for astrophysics*

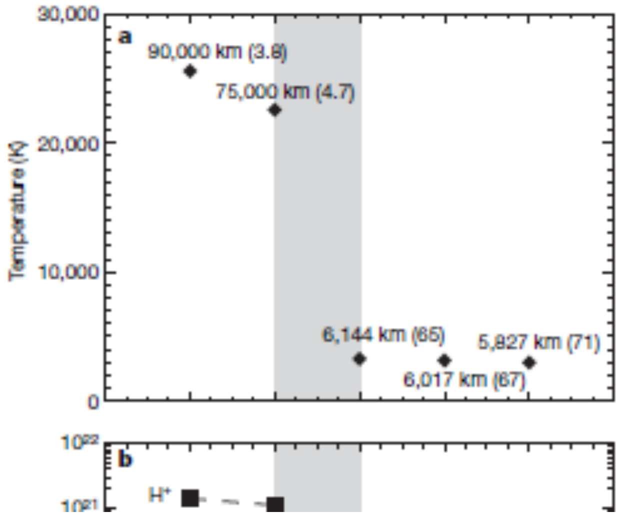
Vol 450 | 6 December 2007 | doi:10.1038/nature06378 nature

LETTERS

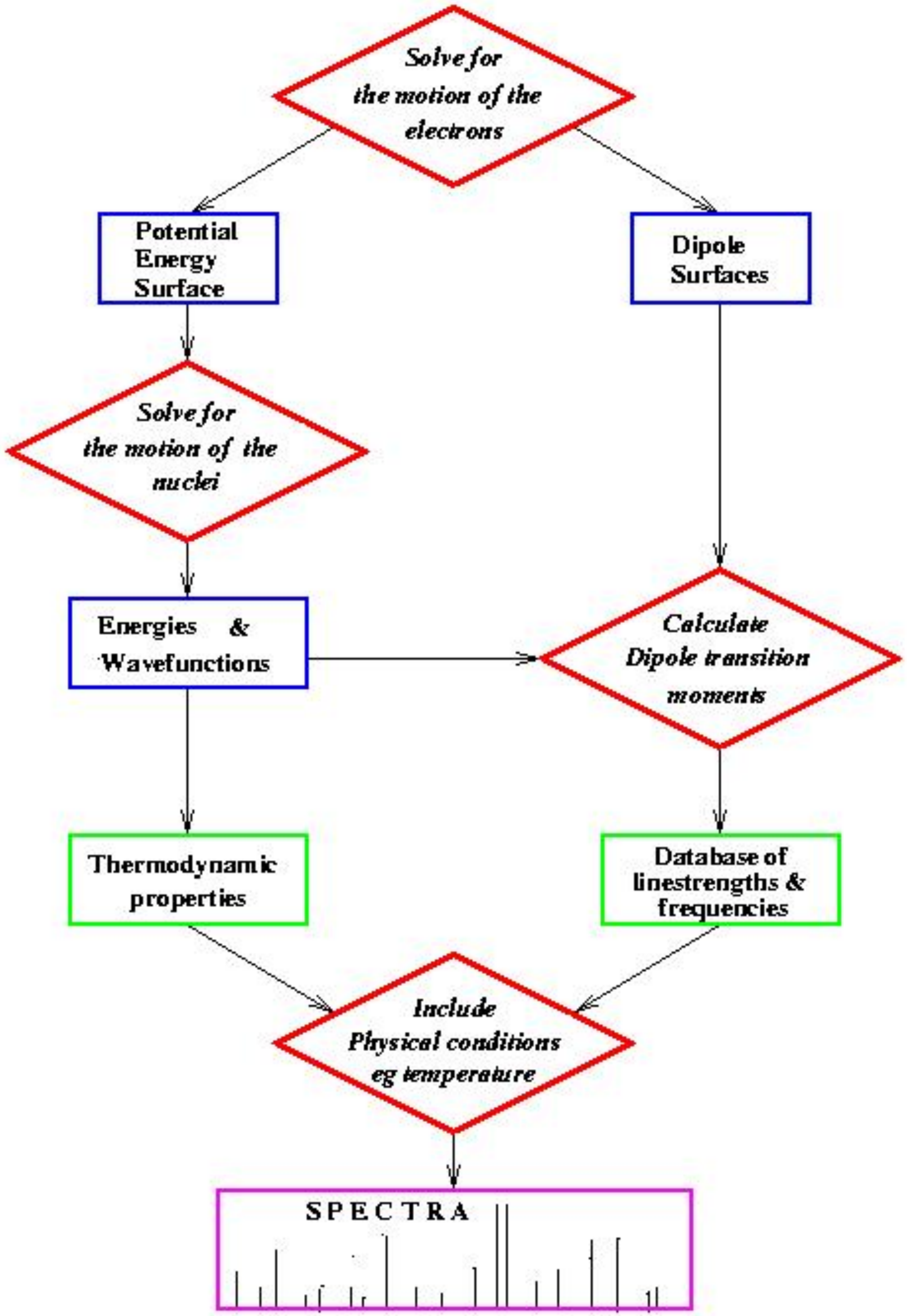
# A stability limit for the atmospheres of giant extrasolar planets

Tommi T. Koskinen[1], Alan D. Aylward[1] & Steve Miller[1]

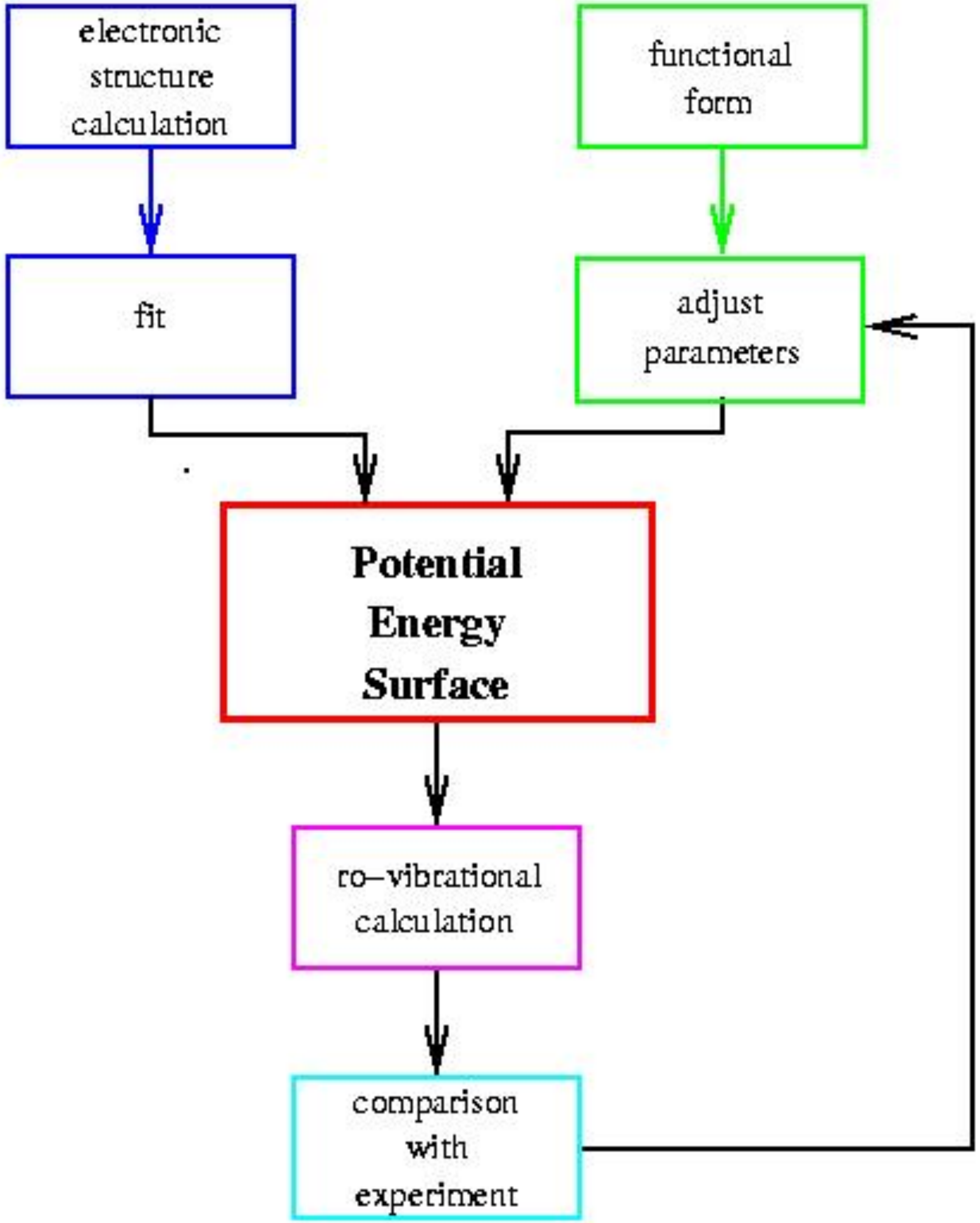
Recent observations of the planet HD209458b indicate that it is surrounded by an expanded atmosphere of atomic hydrogen that is escaping hydrodynamically[1–3]. Theoretically, it has been shown that such escape is possible at least inside an orbit of 0.1 AU (refs 4 and 5), and also that $H_3^+$ ions play a crucial role in cooling the upper atmosphere[5,6]. Jupiter's atmosphere is stable[7], so somewhere between 5 and 0.1 AU there must be a crossover between stability and instability. Here we show that there is a sharp breakdown in atmospheric stability between 0.14 and 0.16 AU for a Jupiter-like planet orbiting a solar-type star. These results are in contrast to earlier modelling[4,8] that implied much higher thermospheric temperatures and more significant evaporation farther from the star. (We use a three-dimensional, time-dependent coupled thermosphere–ionosphere model[6] and properly include cooling by $H_3^+$ ions, allowing us to model globally the redistribution of heat and changes in molecular composition.) Between 0.2 and 0.16 AU cooling by $H_3^+$ ions balances heating by the star, but inside 0.16 AU molecular hydrogen dissociates thermally, suppressing the formation of $H_3^+$ and effectively shutting down that mode of cooling.



# Ab initio calculation of rotation-vibration spectra



# **Potentials:** *Ab initio* or Spectroscopically determined



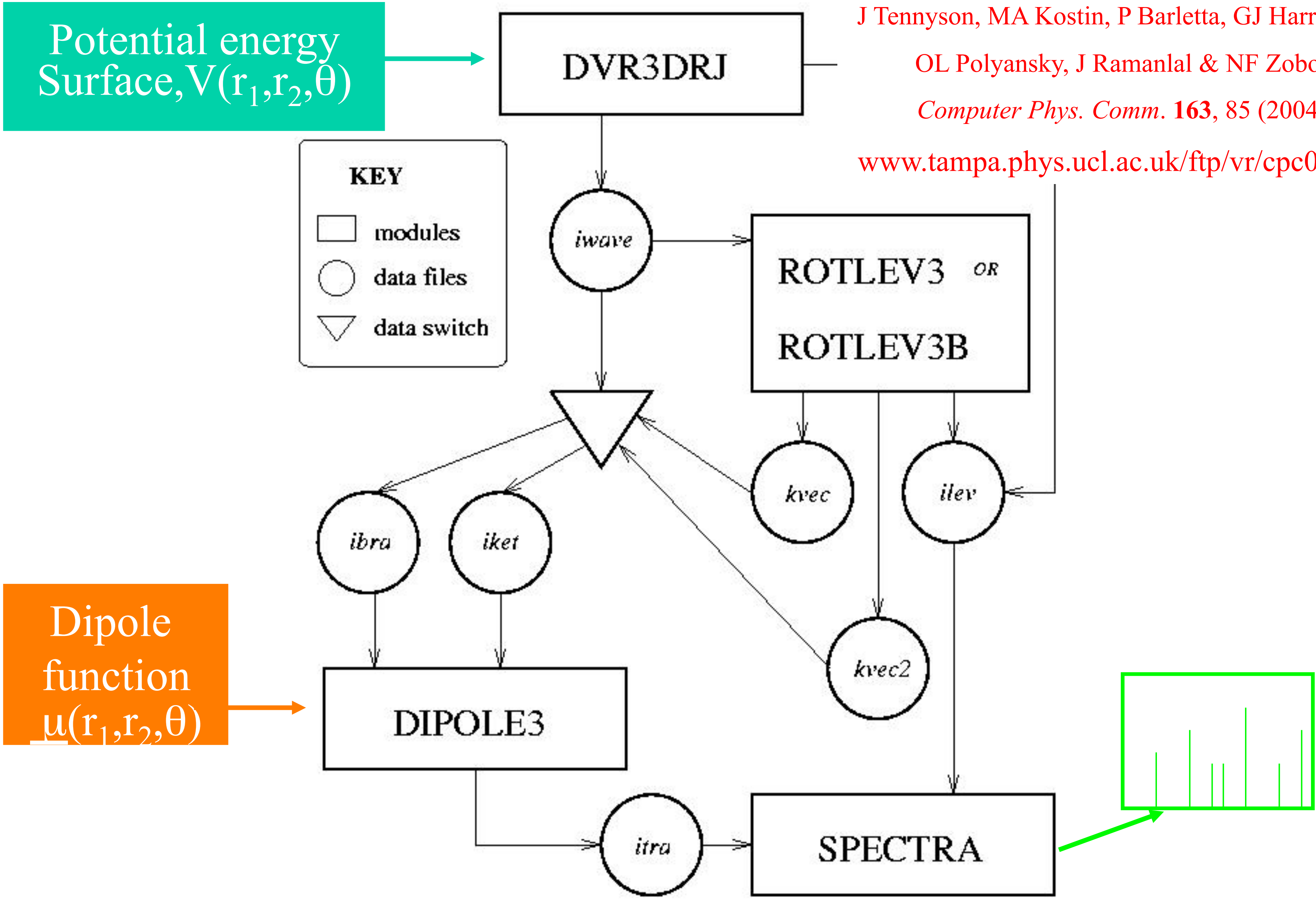
# The DVR3D program suite: triatomic vibration-rotation spectra

J Tennyson, MA Kostin, P Barletta, GJ Harris

OL Polyansky, J Ramanlal & NF Zobov

*Computer Phys. Comm.* **163**, 85 (2004).

www.tampa.phys.ucl.ac.uk/ftp/vr/cpc03



# Computed Water opacity

- Variational nuclear motion calculations
- High accuracy potential energy surface
- *Ab initio* dipole surface

Viti & Tennyson computed **VT2** linelist

Partridge & Schwenke (**PS**), NASA **Ames**

Barber & Tennyson (**BT2**)

Also Ludwig, SCAN, MT, HITEMP .......

# BT2 linelist

Barber et al, MNRAS 368, 1087 (2006).

http://www.tampa.phys.ucl.ac.uk/ftp/astrodata/water/BT2/

- 50,000 processor hours.
- Wavefunctions > 0.8 terabites
- 221,100 energy levels (all to J=50, E = 30,000 $cm^{-1}$)
  14,889 experimentally known
- 506 million transitions (PS list has 308m)
  >100,000 experimentally known with intensities

∀ → Partition function 99.9915% of Vidler & Tennyson's value at 3,000K

**Energy file:**

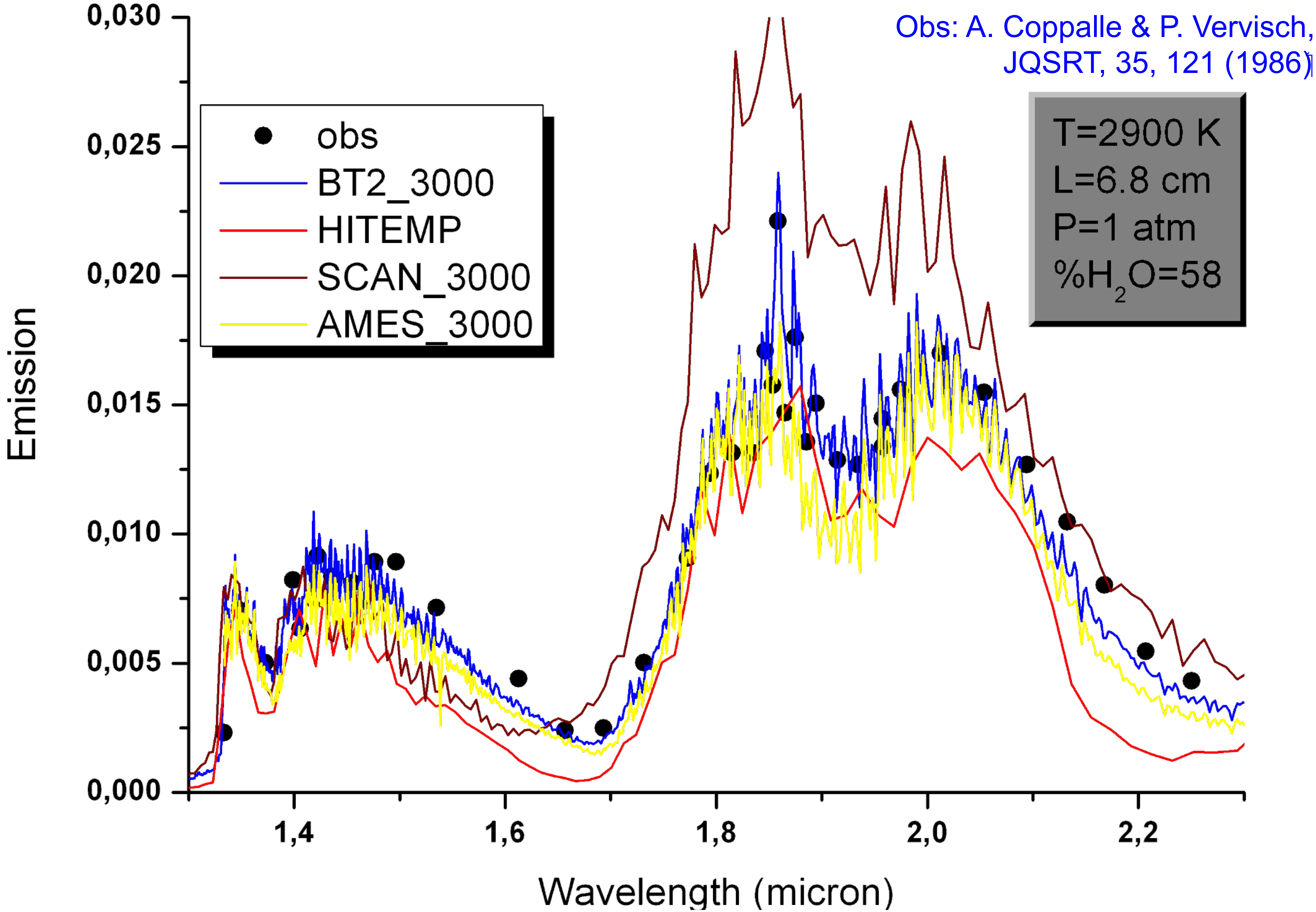
| N | J | sym | n | $E/cm^{-1}$ | $v_1$ | $v_2$ | $v_3$ | J | $K_a$ | $K_c$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 43432 | 11 | 1 | 50 | **8730.136998** | 0 | 2 | 1 | **11** | 3 | 8 |
| 43433 | 11 | 1 | 51 | **8819.773962** | 0 | 4 | 0 | **11** | 6 | 6 |
| 43434 | 11 | 1 | 52 | **8918.536215** | 0 | 0 | 2 | **11** | 2 | 10 |
| 43435 | 11 | 1 | 53 | **8965.496130** | 0 | 2 | 1 | **11** | 5 | 6 |
| 43436 | 11 | 1 | 54 | **8975.145175** | 2 | 0 | 0 | **11** | 4 | 8 |
| 43437 | 11 | 1 | 55 | **9007.868894** | 1 | 0 | 1 | **11** | 3 | 8 |
| 43438 | 11 | 1 | 56 | **9082.413891** | 1 | 2 | 0 | **11** | 6 | 6 |
| 43439 | 11 | 1 | 57 | **9170.343871** | 1 | 0 | 1 | **11** | 5 | 6 |
| 43440 | 11 | 1 | 58 | **9223.444158** | 0 | 0 | 2 | **11** | 4 | 8 |
| 43441 | 11 | 1 | 59 | **9264.489815** | 2 | 0 | 0 | **11** | 6 | 6 |
| 43442 | 11 | 1 | 60 | **9267.088316** | 0 | 5 | 0 | **11** | 2 | 10 |
| 43443 | 11 | 1 | 61 | **9369.887722** | 0 | 2 | 1 | **11** | 7 | 4 |
| 43444 | 11 | 1 | 62 | **9434.002547** | 0 | 4 | 0 | **11** | 8 | 4 |
| 43445 | 11 | 1 | 63 | **9457.272655** | 1 | 0 | 1 | **11** | 7 | 4 |
| 43446 | 11 | 1 | 64 | **9498.012728** | 0 | 0 | 2 | **11** | 6 | 6 |
| 43447 | 11 | 1 | 65 | **9565.890023** | 1 | 2 | 0 | **11** | 8 | 4 |

# Transitions file:

**12.8 Gb**

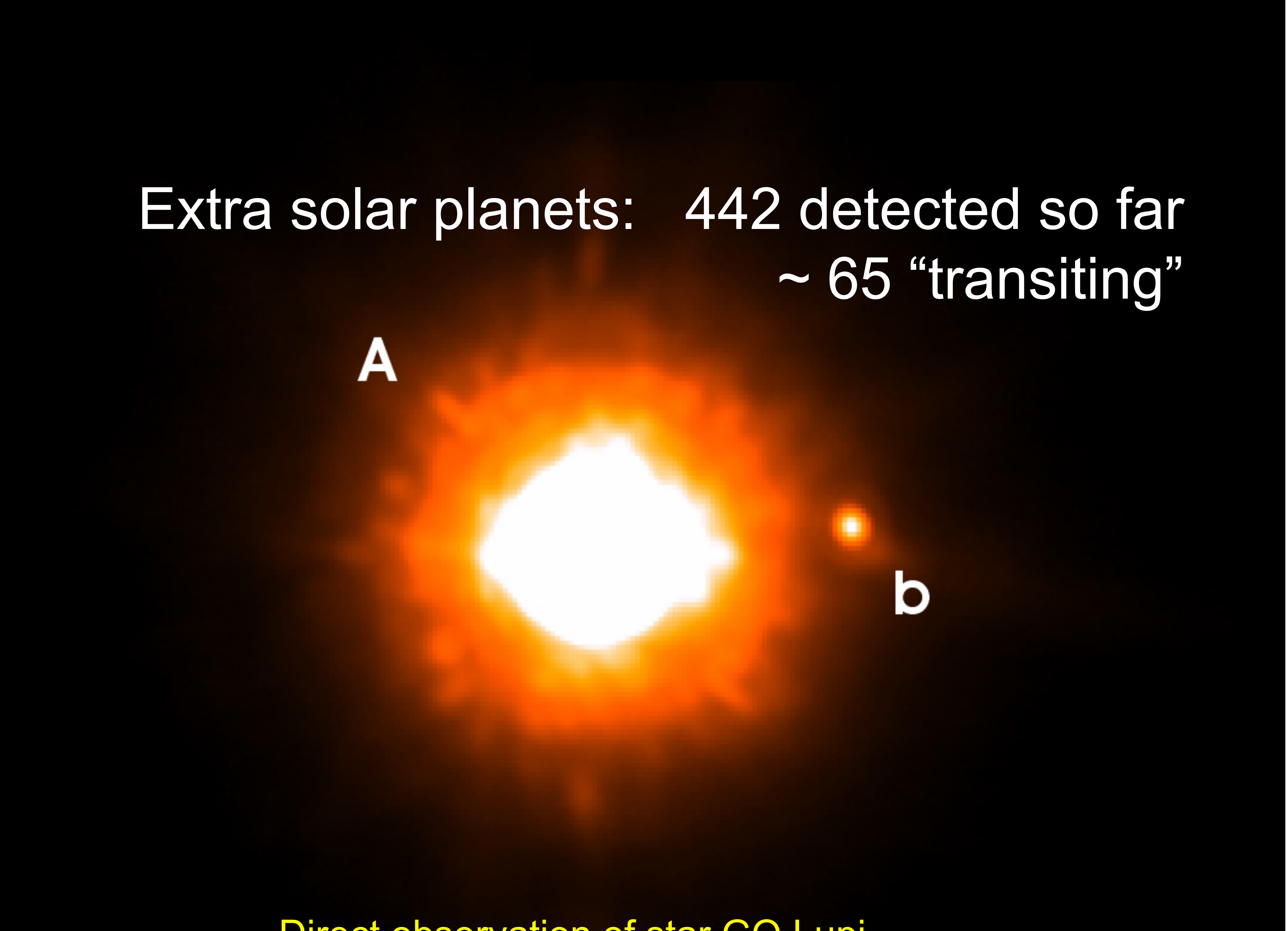
Divided into
16 files by frequency
for downloading

| $N_f$ | $N_i$ | $A_{if}$ |
|---|---|---|
| 144848 | 146183 | 3.46E-04 |
| 115309 | 108520 | 7.42E-04 |
| 196018 | 198413 | 1.95E-04 |
| 7031 | 7703 | 1.13E-02 |
| 149176 | 150123 | 1.69E-04 |
| 81528 | 78734 | 2.30E-01 |
| 80829 | 78237 | 8.83E-04 |
| 209672 | 210876 | 2.51E-01 |
| 207026 | 203241 | 2.72E-04 |
| 188972 | 184971 | 1.25E-01 |
| 152471 | 153399 | 1.12E-02 |
| 39749 | 37479 | 1.46E-07 |
| 10579 | 15882 | 6.90E-05 |
| 34458 | 35617 | 1.15E-03 |

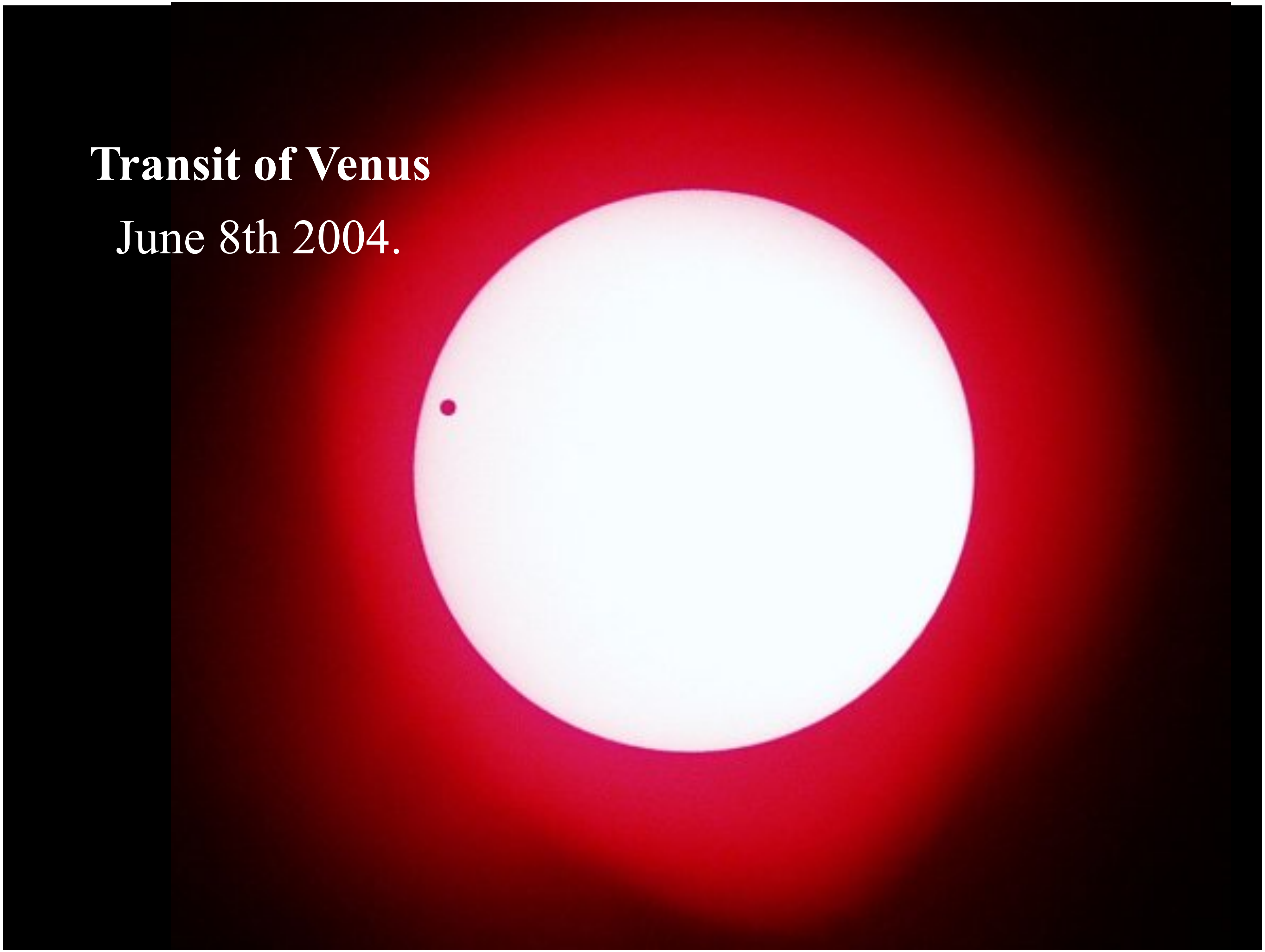



**New edition of HITEMP**: LS Rothman, IE Gordon, RJ Barber, H Dothe, RR Gamache, A Goldman, VI Perevalov, SA Tashkun + J Tennyson, JQSRT (in press)

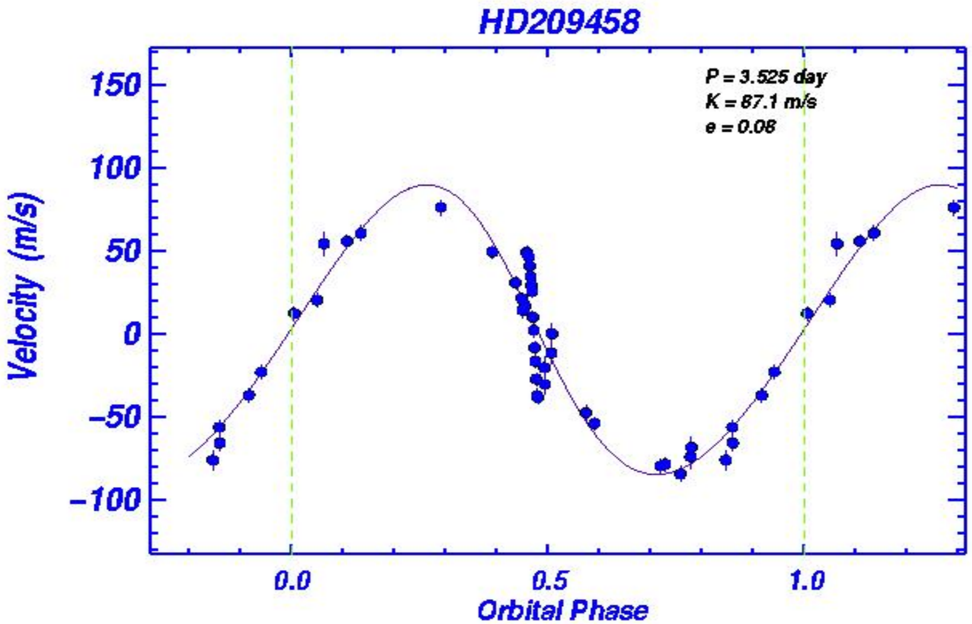
Extra solar planets: 442 detected so far
~ 65 “transiting”

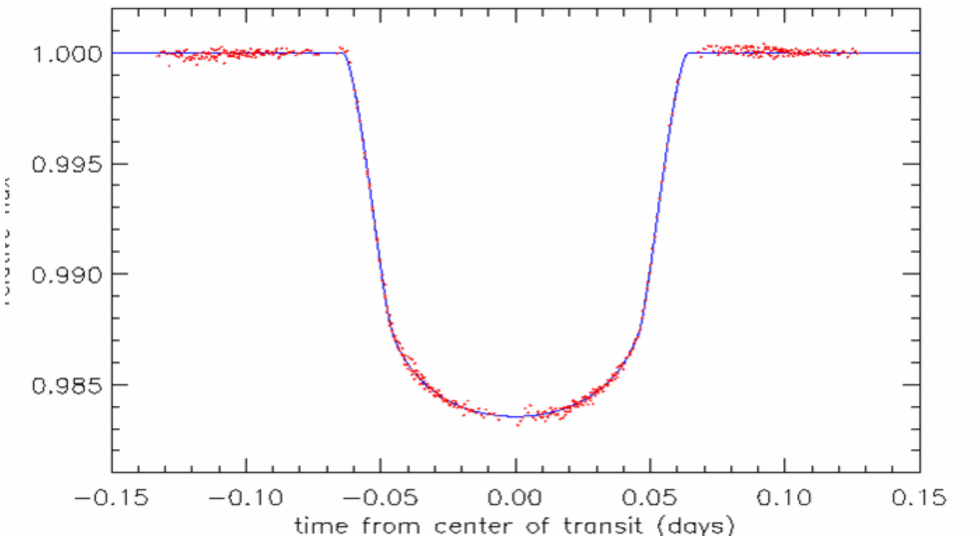



Direct observation of star GQ Lupi


Transit of Venus
June 8th 2004.

# HD 209458b



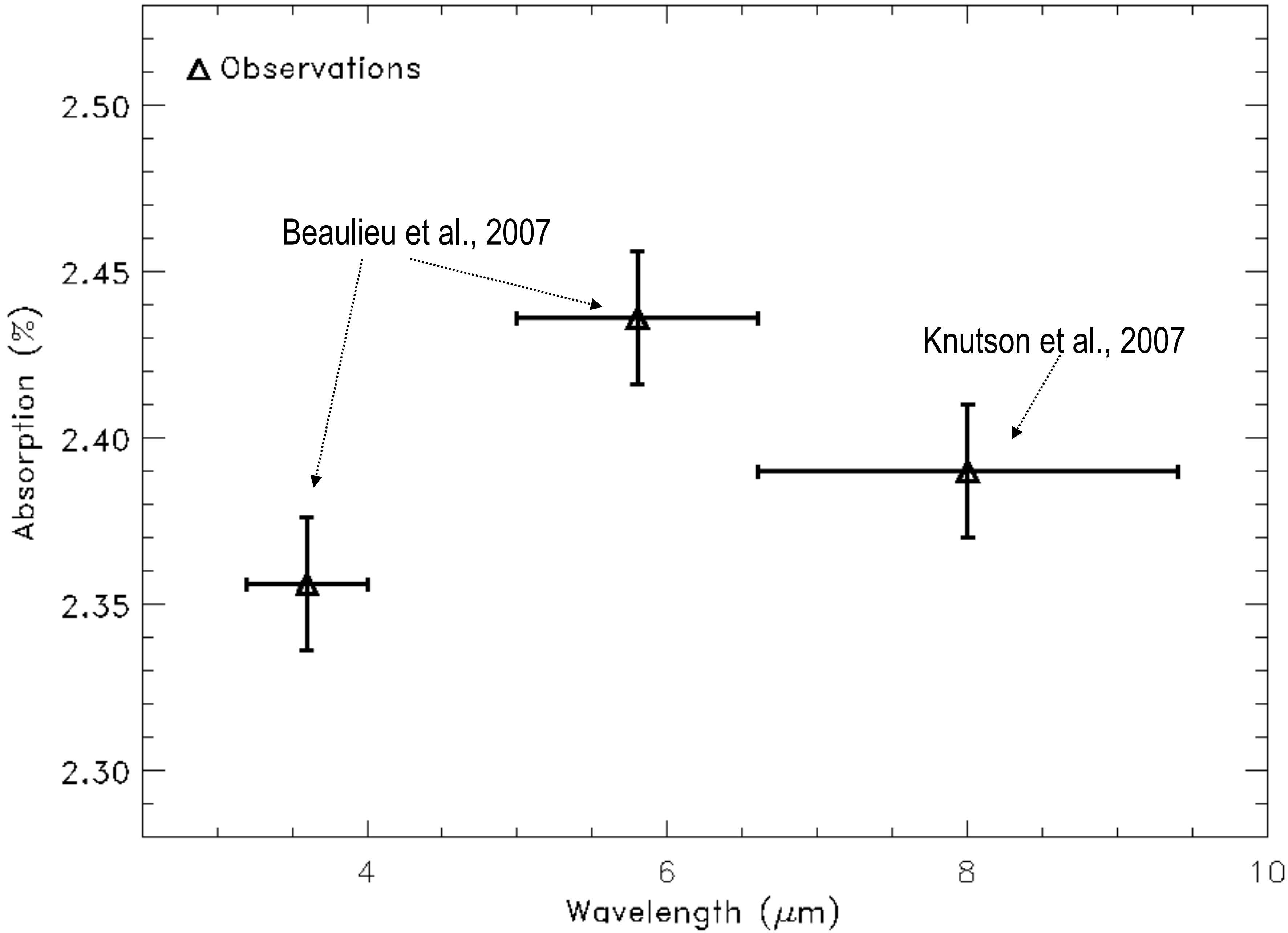

Period = 3.524738 days

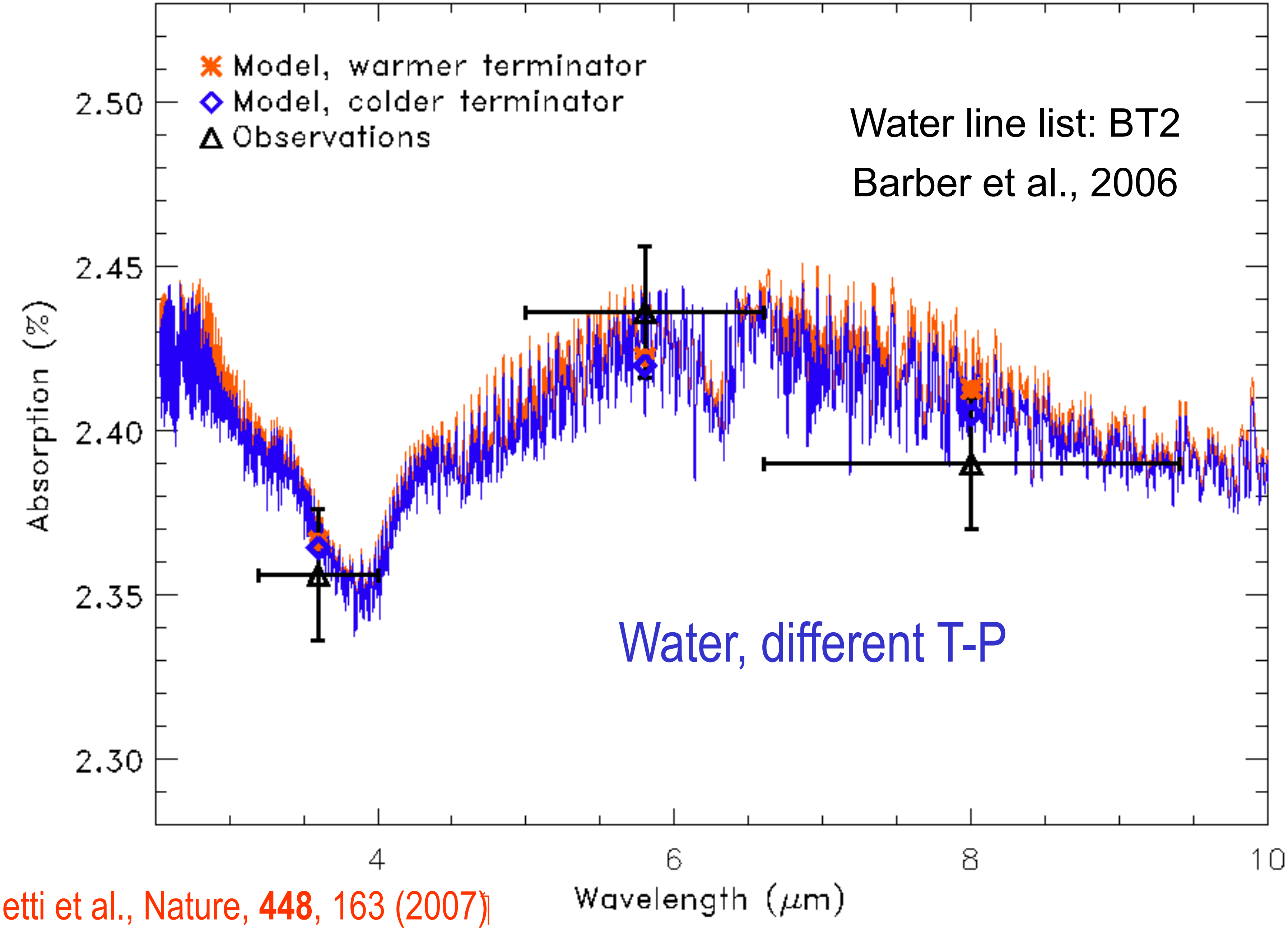
Mass = 0.69 ±0.05 $M_{Jupiter}$

Radius = 1.35 ±0.04 $R_{Jupiter}$

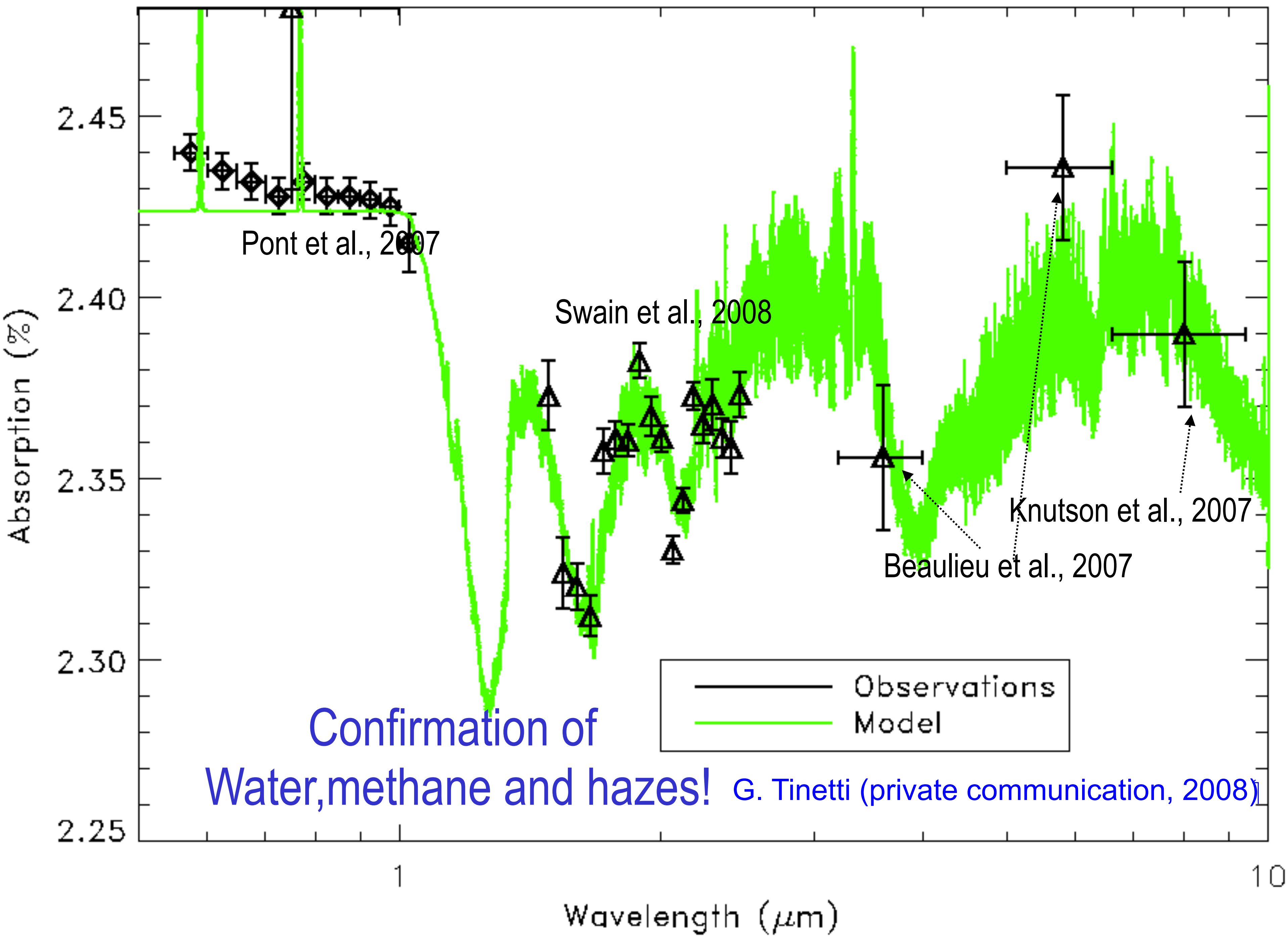
Density = 0.35 ±0.05 $g/cm^3$

# Primary transit + IR + Spitzer






Tinetti et al., Nature, **448**, 163 (2007)



Pont et al., 2007
Swain et al., 2008
Knutson et al., 2007
Beaulieu et al., 2007
Observations
Model
Confirmation of
Water,methane and hazes!
G. Tinetti (private communication, 2008)
Absorption (%)
Wavelength (μm)
2.45
2.40
2.35
2.30
2.25
1
10

# Why is ammonia of interest?

- Present in: ISM, molecular clouds, late-type dwarfs, gas giants, exoplanets, comets etc.

- $NH_3$, $CH_4$, $H_2O$ etc. in the spectra of exoplanets give additional information about P and T. $NH_3$ also gives information about nitrogen chemistry.

- Accurate modelling of the atmospheres of late-type brown dwarfs.

- Y-dwarfs (search is on) are characterised by $NH_3$

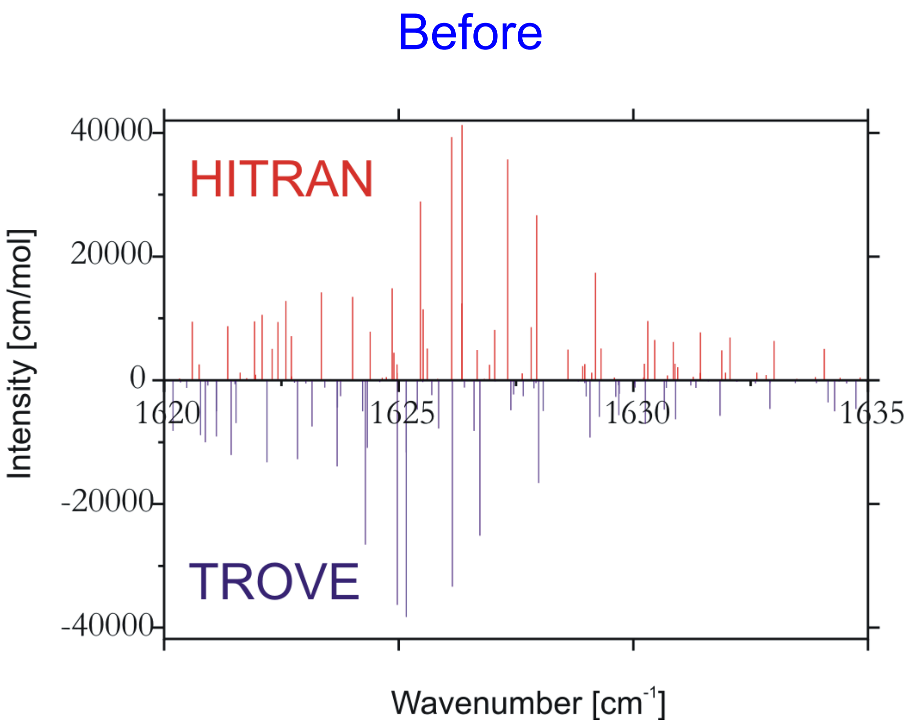
# Ammonia linelist

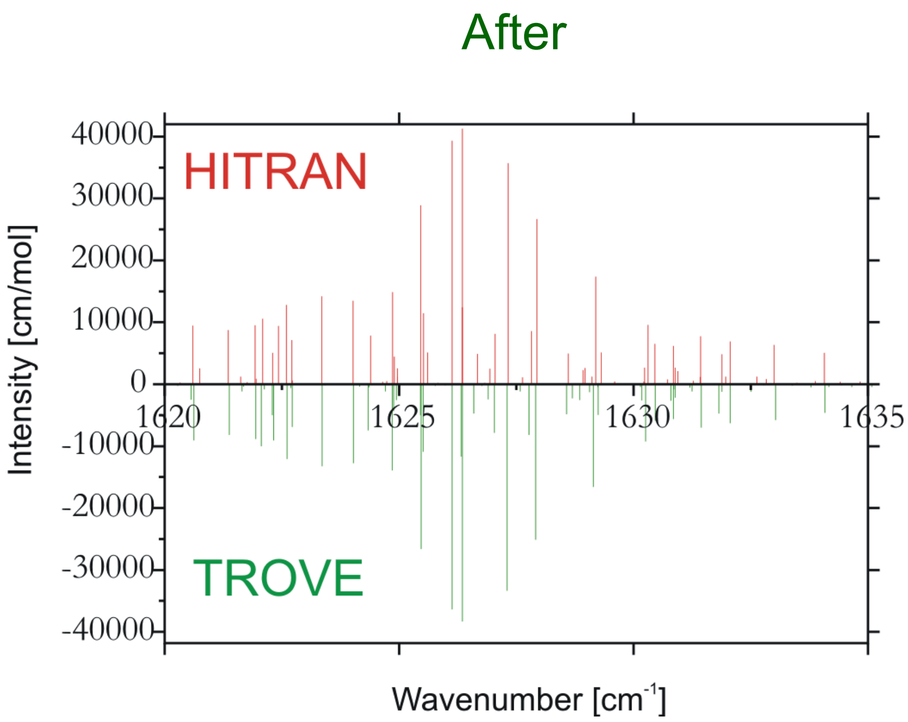
**Cold** (ie $T < 300$ K). Levels up to $J=12$, $E < 12000$ cm$^{-1}$

TROVE nuclear motion program, spectroscopic potential

S.N. Yurchenko, R.J. Barber, A. Yachmenev, W. Theil, P. Jensen & J. Tennyson,
J. Phys. Chem. A, 113, 11845 (2009).

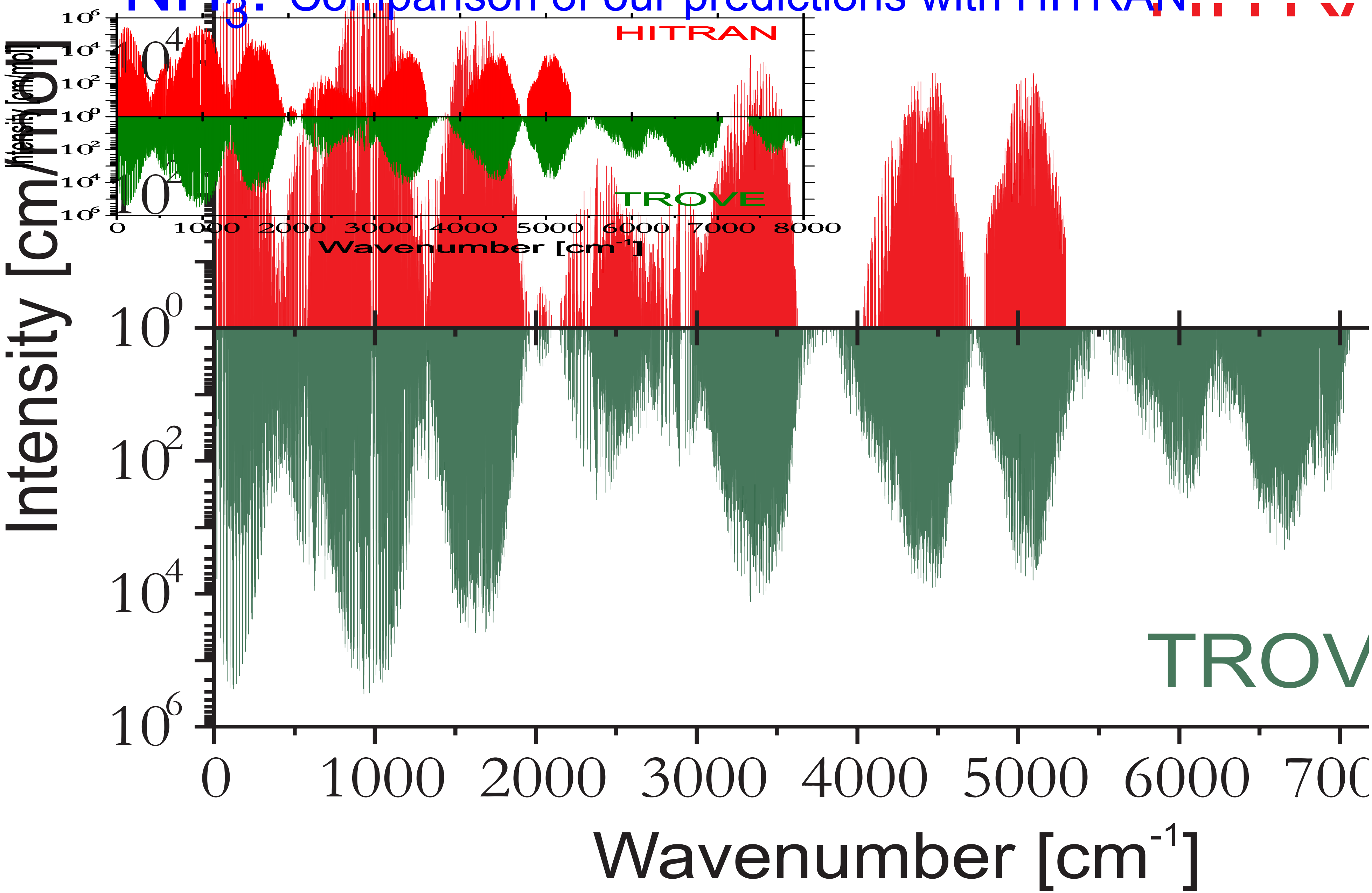
# Fine tuning potential




Refinement of the PES: Very elaborate

# $NH_3$: Comparison of our predictions with HITRAN




).

# Problems with ammonia in Hitran2000/2004/2008

| Problem | No. Identified | No. Resolved |
|---|---|---|
| Symmetry labels wrong | 933 | 929 |
| Forbidden transitions | 262 | 0 |
| Lower state inconsistencies | 250 | 248 |
| Upper state inconsistencies | 271 | 230 |
| Remaining inconsistencies (all $2v_2$) | 41 | 41 |
| | | |
| Incompletely assigned | 2684 | 0 |

Michael Down (UCL)

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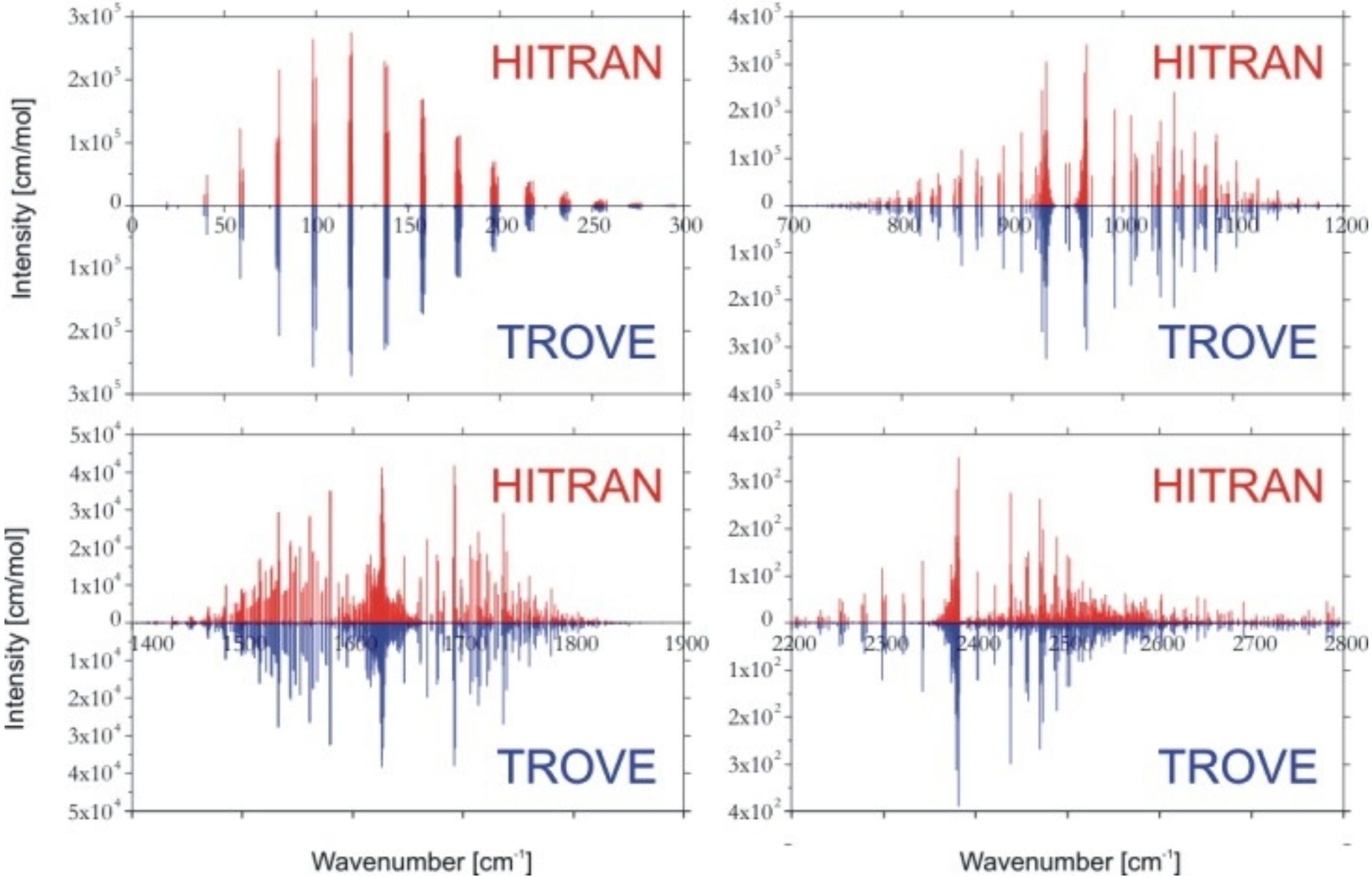



S.N. Yurchenko, R.J. Barber, A. Yachmenev, W. Theil, P. Jensen & J. Tennyson,
J. Phys. Chem. A, 113, 11845 (2009).

# Ammonia linelists

**Cold** (ie T < 300 K). Levels up to J=12, E <12000 $cm^{-1}$

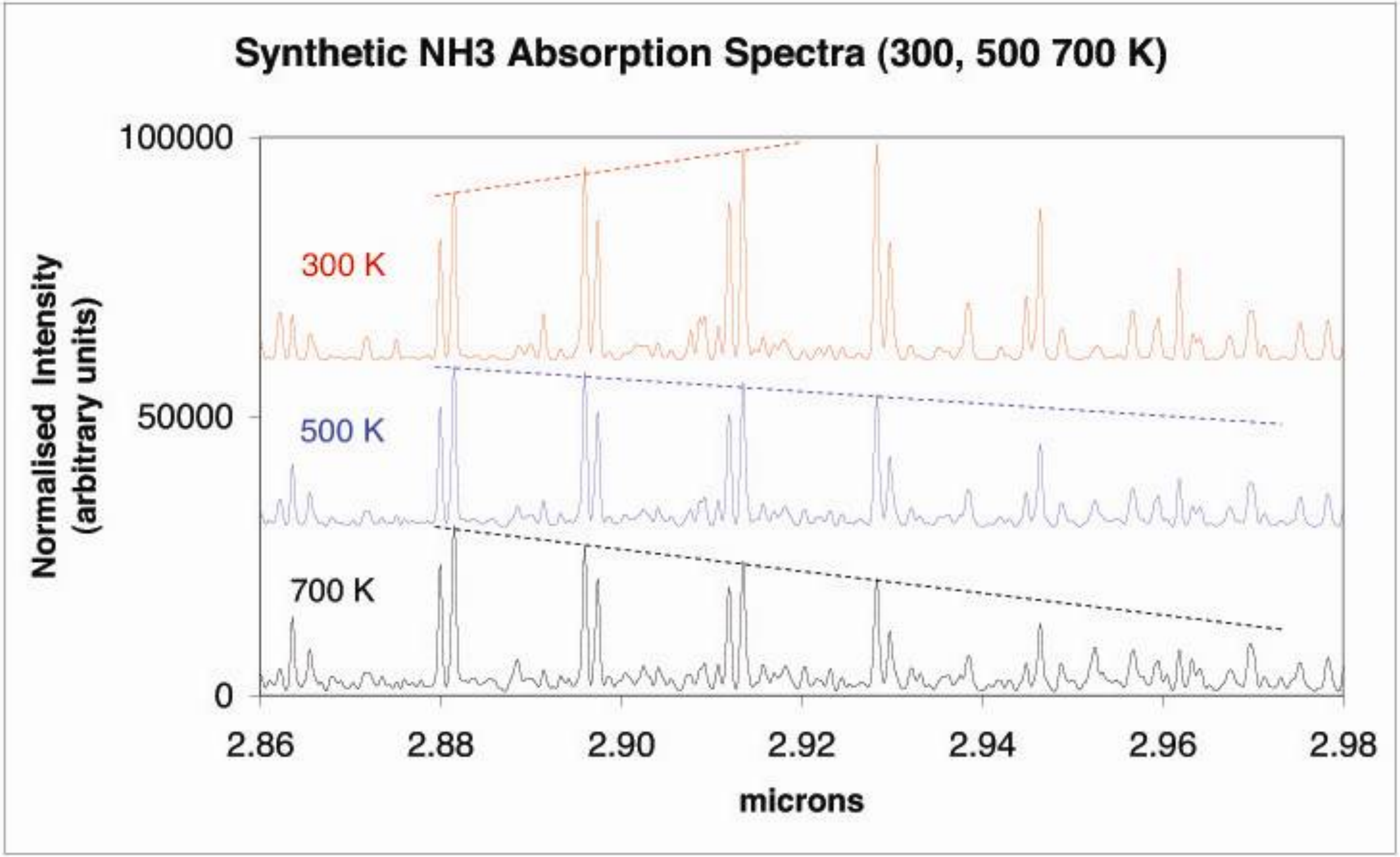
TROVE nuclear motion program, spectroscopic potential

S.N. Yurchenko, R.J. Barber, A. Yachmenev, W. Theil, P. Jensen & J. Tennyson,
J. Phys. Chem. A, 113, 11845 (2009).

**Hot** (ie T ~ 1500 K). Levels up to J=30, E <12000 $cm^{-1}$

Improved spectroscopic potential, 1 124 388 206 lines

S.N. Yurchenko, R.J. Barber & J. Tennyson , MNRAS (to be submitted)



Synthetic NH3 Absorption Spectra (300, 500 700 K)
Normalised Intensity (arbitrary units)
100000
50000
0
300 K
500 K
700 K
2.86
2.88
2.90
2.92
2.94
2.96
2.98
microns

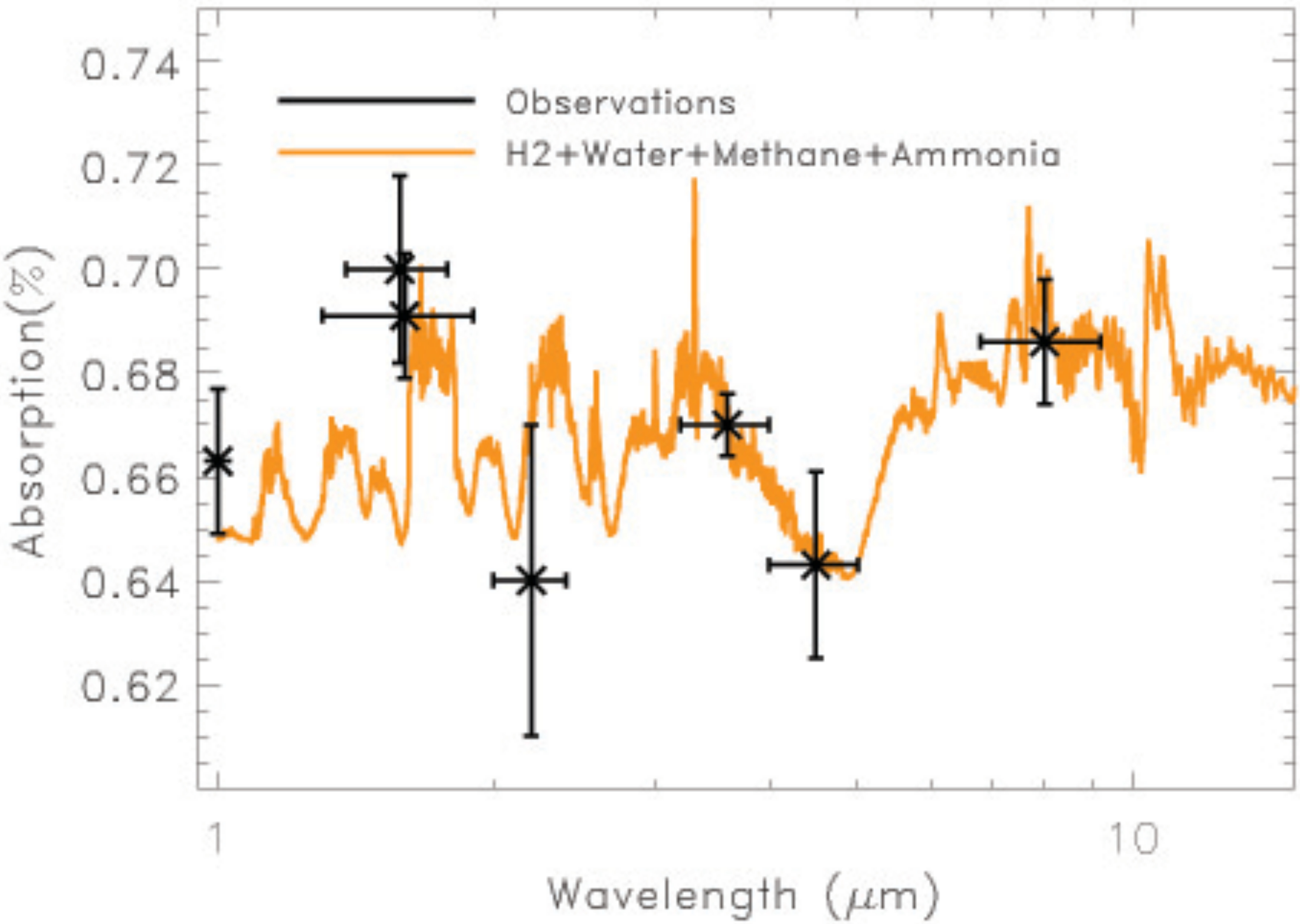
# Ammonia linelists: hot initial applications

1. Ultra cool (T ~ 520 +/- 40 K) brown dwarf, UGPSJ0722-0540
   T9 dwarf, no ammonia observed
   (Discovery of a very cool, very nearby brown dwarf in the Galactic plane
   P Lucas et al, arXiv:1004:0317 and MNRAS submitted)

2. Exoplanet GJ436b : a transiting "super Neptune", also T ~ 500 K

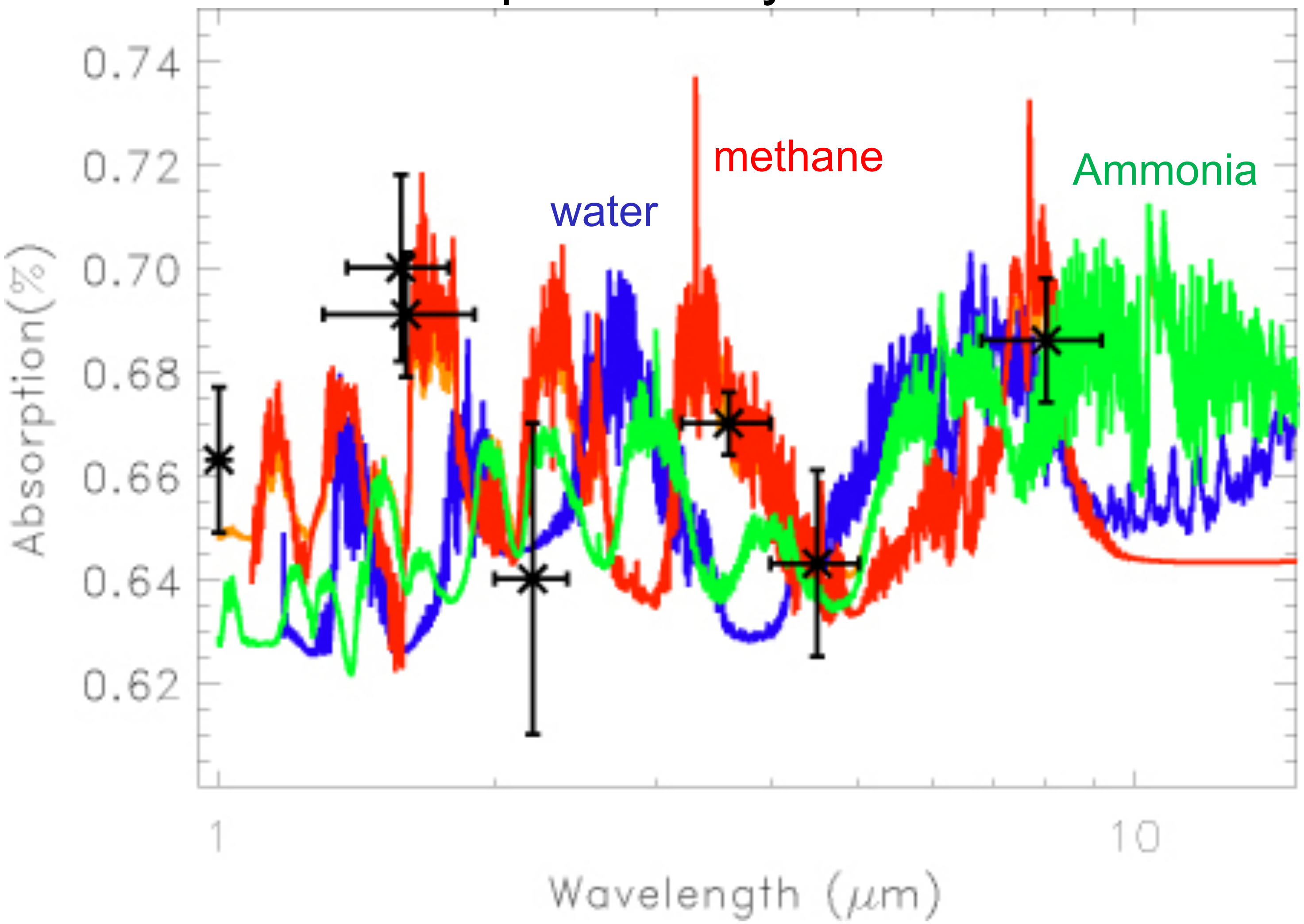
3. Analysis of hot Lab spectra from University of York: 570 K < T < 1500 K.

# Spitzer observations of exoplanet GJ436b




J-P Beaulieu et al, Astrophys. J. (submitted)

# GJ436b spectrum by molecule




J-P Beaulieu et al, Astrophys. J. (submitted)

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- Hydrocarbons: $C_2H_4$, $C_2H_6$, others?
- Dust (other biomarkers eg $HNO_3$?)

# Linelists completed or under construction @ UCL by

$H_3^+$ Liesl Neale ($H_2D^+$ Taha Sochi)

$H_2O$ Bob Barber (HDO Boris Voronin)

HCN/HNC ($H^{13}CN$/ $H^{13}CN$) Greg Harris

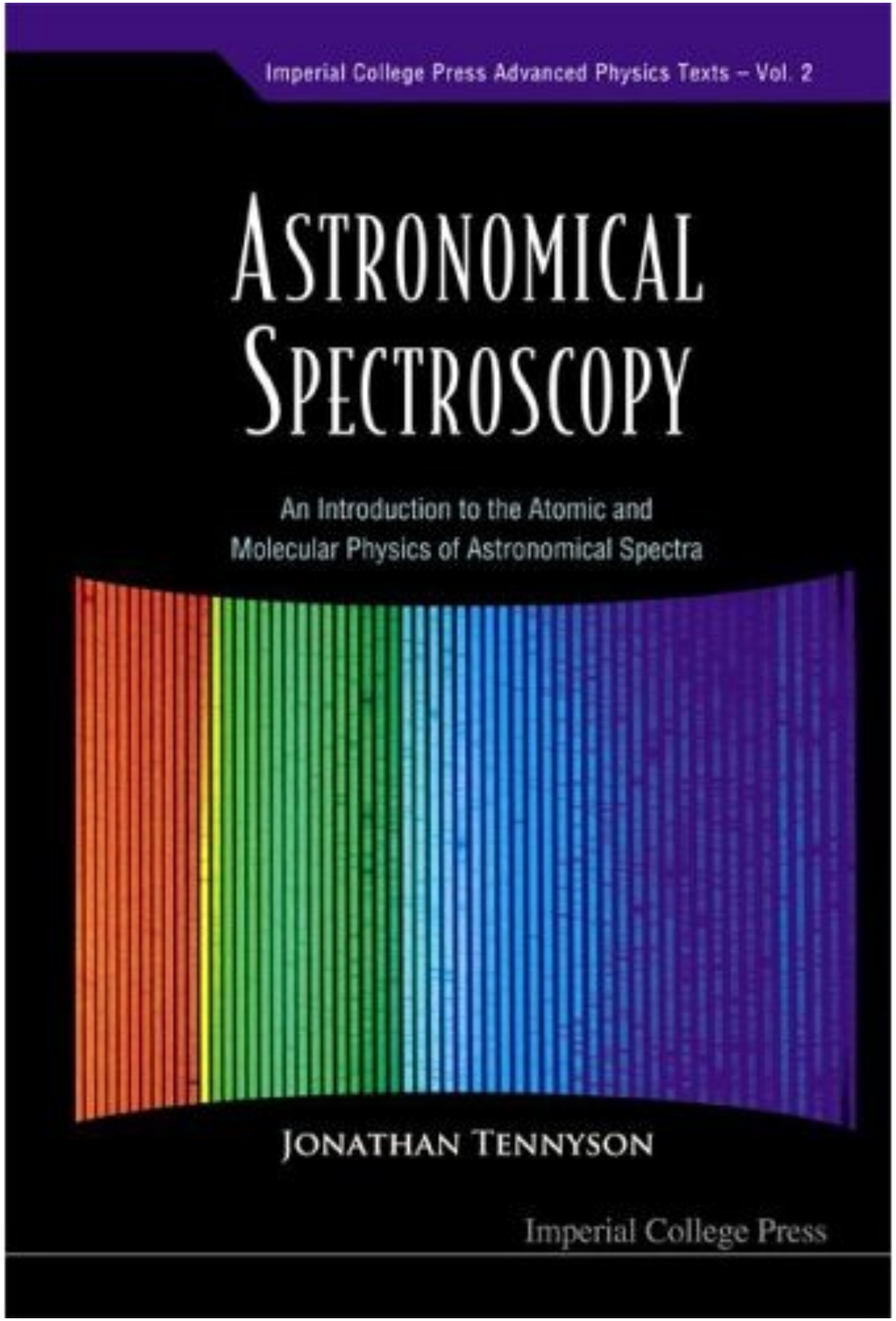
$HeH^+$ Elodie Engel

$NH_3$ Bob Barber and Sergei Yurchenko (Dresden)

HCCH Andrea Urru

www.exomol.com

$C_3$ Santina La Delfa and Taha Sochi




www.worldscibooks.com/physics/p371.html

*"The best book for anyone who is embarking on research in astronomical spectroscopy"*
Contemporary Physics (2006)