PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Water in exoplanets

Giovanna Tinetti, Jonathan Tennyson, Caitlin A. Griffith and Ingo Waldmann

Phil. Trans. R. Soc. A 2012 **370**, 2749-2764
doi: 10.1098/rsta.2011.0338

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A

Phil. Trans. R. Soc. A (2012) **370**, 2749–2764
doi:10.1098/rsta.2011.0338

Water in exoplanets

By Giovanna Tinetti[1,]*, Jonathan Tennyson[1], Caitlin A. Griffith[2] and Ingo Waldmann[1]

[1]*Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK*
[2]*LPL, University of Arizona, Tucson, AZ, USA*

Exoplanets—planets orbiting around stars other than our own Sun—appear to be common. Significant research effort is now focused on the observation and characterization of exoplanet atmospheres. Species such as water vapour, methane, carbon monoxide and carbon dioxide have been observed in a handful of hot, giant, gaseous planets, but cooler, smaller planets such as Gliese 1214b are now analysable with current telescopes. Water is the key chemical dictating habitability. The current observations of water in exoplanets from both space and the ground are reviewed. Controversies surrounding the interpretation of these observations are discussed. Detailed consideration of available radiative transfer models and linelists are used to analyse these differences in interpretation. Models suggest that there is a clear need for data on the pressure broadening of water transitions by H_2 at high temperatures. The reported detections of water appear to be robust, although final confirmation will have to await the better quality observational data provided by currently planned dedicated space missions.

Keywords: exoplanets; water vapour; pressure broadening; atmospheric models; linelists

1. Introduction

Before 1995 only nine planets were known. These comprised our Solar System including our own planet, the Earth, and Pluto, subsequently reclassified, in 2006, as a 'dwarf' planet. Before 1995, planets were divided in giants and terrestrials: the former colder, with reducing atmospheres, and the latter warmer, smaller, denser and with oxidizing atmospheres. The Solar System model, with planets moving around the Sun on quasi-circular and coplanar orbits, appeared to be the unquestioned paradigm, blessed by Kant's and Laplace's theories of planet formation. Prior to the mid-1990s, stellar astronomers and planetologists did not talk to each other very often: stars, being nuclear burning objects, classified by mass and luminosity according to the Hertzsprung–Russell (H-R) diagram, seemed to have little in common with planets. But all this was before Mayor & Queloz [1] found a gas-giant planet orbiting the G-type star 51 Peg with an annual period of only four Earth-days.

*Author for correspondence (g.tinetti@ucl.ac.uk).

One contribution of 17 to a Theo Murphy Meeting Issue 'Water in the gas phase'.

Seven hundred plus planets later [2]—not including the approximately 1200 planetary candidates detected by Kepler [3]—our Solar System seems to stand out more as a rarity than the paradigm in our Galaxy. While better statistics and planet detections with multiple discovery methods are needed to eliminate the undoubted bias in the current sample owing to the detection techniques adopted, most of the gas giant planets detected so far orbit very close to their parent star. It seems likely that they migrated close to their star during the formation process, which means that our Jupiter, at 5 AU from the Sun, seems to have experienced an unusual history [4] compared with the observed population of hot-Jupiters. Similarly, eccentric planets no longer appear to be oddities. Furthermore 'super-Earths', planets up to 10 Earth masses, are common around other stars [5,6], but completely absent in our Solar System. These are hircocervi between Neptunic and telluric planets, and about which we know little today. The 'exoplanet revolution' has indeed changed irreversibly our views about planets and stars, and the ways in which they are formed.

A critical milestone in our understanding of these faraway objects was the realization that we can probe the atmospheres of a subset of known exoplanets: those which transit their parent star when viewed from Earth. For those planets, one can effectively use the wavelength-dependent stellar occultation to measure a transmission spectrum of the planetary limb [7], or use the star as a 'natural coronograph' while the planet is passing behind it, to extract a spectrum emitted or reflected by the planet [8,9]. Additionally, one can observe the planet at different orbital phases [10–14].

Indeed transit spectroscopy has proved to be very successful in the last 10 years: the use of the transit technique combined with the photometric precision of the Hubble and Spitzer Space Telescopes has allowed a glimpse of the atmospheric composition, albedo, escape processes and thermal characteristics of a handful of hot-Jupiters (e.g. [15–24]), as well as those of colder and smaller planets, such as the warm Neptune GJ436b [25,26].

More recently, ground-based telescopes have been combined powerfully to space-based observations. Ground-based observations have the non-trivial limitation of having the Earth's atmosphere interfering with the measurement, especially in the IR, where key molecules show stronger spectral features. At the same time, observations from the ground have the great advantage of being repeatable more easily and of offering higher spectral resolution than Hubble and Spitzer in some spectral channels. Techniques relying on the absolute subtraction of telluric atmospheric signals from one or a few high signal-to-noise exoplanetary spectra have not yielded a conclusive detection to date [27–31]. Such techniques are, in fact, dependent on a theoretical model of the Earth's atmosphere that needs to be accurate at least at the level of a few parts in 10 000: this accuracy is very hard to achieve given the highly variable telluric contribution throughout an observing run. By contrast, techniques based on time-resolved coverage of the eclipse event, providing lightcurves at multiple wavelengths (low spectral R) or time-dependent Doppler shift signatures (high spectral R), have in common that they are relative measurements, so they rely less on the absolute correction of the telluric signal. Using these methods, there has been a rapid escalation in ground-breaking results in the past few years: results include the detection of alkali metals in the optical [32–35], and the first detection and atmospheric characterization of the warm super-Earth GJ1214b [36,37]. In the near-IR (NIR), stand out the detection of CO [38], never conclusively detected from space, and the non-local thermodynamic equilibrium methane emission [39], completely unexpected. In response to the concerns raised by Mandel *et al.* [31], Waldmann *et al.* [40] have demonstrated the reproducibility of the methane emission feature in several observations, and shown that the data-analysis method is robust enough to remove the telluric contamination while preserving the exoplanetary signal.

After almost 10 years of successes in the field of exoplanet atmosphere characterization, the time has come to look back, critically, at what has been achieved to help prepare for an even brighter future. In this work, we specifically consider the role of the key water molecule in the atmospheres of exoplanets. We begin by summarizing the brief history of water vapour observations in exoplanets; we then present our exoplanet model; comparisons are made between this model and the input spectroscopic data for water vapour with other studies.

2. Water detection in the atmosphere of an extrasolar planet

Water (H_2O) is made from the two most abundant chemically reactive elements in the universe, and it is the necessary ingredient for all types of life found on Earth. The importance of water as a condensable and chemically active species in protoplanetary discs has long been emphasized in planetary literature. The time-varying location at which water is saturated in a formal thermodynamic sense—the snow line—can be considered the dividing line between the inner and outer Solar System. For planets at orbital distances $\leq$1 AU, H_2O is expected to be one of the most abundant atmospheric components. For all these reasons, water vapour was the most sought after molecule in the atmosphere of an exoplanet.

In early 2007, three different teams published, nearly simultaneously, the first exoplanetary emission spectra observed with the Spitzer-IRS spectrograph in the wavelength region approx. 7–14.5 μm [41–43]. The contribution of water vapour in these rather noisy spectra did not appear obvious, and several articles tried to explain the published results and the potential absence of water vapour in the atmospheres of hot-Jupiters. Contradicting these results, Barman [44] proposed that a spectral feature at about 1 μm in the visible (VIS) spectrum of HD 209458b [15] was caused by water vapour absorption. Tinetti *et al.* [45] proposed searching for water vapour using IR differential band photometry, i.e. by observing simultaneously the primary transit at multiple wavelengths in the IR. The rationale being that water vapour has a stronger signature in the IR than the VIS, and transit spectra can be interpreted with less ambiguity than emission spectra, because they are far less sensitive to atmospheric vertical thermal gradients.

Observations of the primary transit of HD 189733b were performed with the Spitzer-IRAC camera simultaneously at 3.6 μm, 4.5 μm [46] and 8 μm [11]. We interpreted these combined observations at 3.6, 5.8 and 8 μm as highly suggestive of water vapour absorbing in the atmosphere of HD 189733b [16]. The model adopted by Tinetti *et al.* [45] is detailed below. Tinetti *et al.* [16] used this model and geometry, but adopted the BT2 linelist [47] as the source of water opacities; whereas Tinetti *et al.* [45] used the Wattson & Rothman [48] linelist given in HITEMP 1991. The BT2 linelist gave, almost effortlessly, a fit to the

HD 189733b IRAC observations, whereas HITEMP 1991 contained cutoffs that limit the ability of the linelist to capture the discrepancy observed between 3.6 and 5.8 μm. This issue is also discussed below.

Confirmation of the presence of water vapour in the atmosphere of HD 189733b was provided by NIR and mid-IR (MIR) observations using Hubble-NICMOS [18,20] and Spitzer-IRAC/IRS [21,49]. Primary transit and secondary eclipse observations were repeated for HD 209458b in the NIR–MIR with NICMOS and IRAC/IRS [19,50,51]. All these datasets can be explained by models assuming water as one of the key atmospheric components (see also [52–57]). On the contrary, hazes or clouds seem to affect the transparency of the atmosphere in the visible–NIR spectral range, at wavelengths shorter than approx. 1.5 μm. While this is the case for HD 189733b and HD 209458b [15,58,59], the hot-Jupiter XO-1b spectrum shows distinctive molecular features, among which those of water, in the 1.2–1.8 μm spectral region [17].

The claimed detection of water in exoplanets, while apparently confirmed by a number of observations, different instruments and several observational teams, is not uniformly accepted. In this context, we would make the following comments.

While we are comfortable with the statement that water vapour has been detected in a handful of exoplanets' atmospheres, we are uneasy about attempts to retrieve water vapour absolute abundances in all these cases. The level of degeneracy associated with low-resolution spectra, or even photometric bands, is far from negligible [19,57,60,61]. As explained by Tinetti *et al.* [62], this degeneracy, which can only be resolved by simultaneous broader spectral range and preferably higher resolution observations, has different origins in transit and emission spectra.

The amount of water on exoplanets has been debated [63–65]. Most recently, Gibson *et al.* [65] questioned the validity of using NICMOS to acquire exoplanet spectra at the level of accuracy needed to sound the atmospheric features. We believe instead that the temporal stability of NICMOS, in its G206 grism setting, is among the highest of the past and current IR instruments available, and the systematic noise owing to the instrument can be adequately removed with a parametrization of the instrument state vectors [18,66]. In a more recent article Gibson *et al.* [67] have obtained results consistent to Swain *et al.* [18] using a different analysis technique. The most obvious approach would be to repeat the original observations to characterize the observational data beyond any reasonable doubt. Unfortunately, with the loss of NICMOS and Spitzer-IRS/MIPS and partially IRAC, this is technically impossible at present from space. Nonetheless, the concerns expressed by Gibson *et al.* [65] are easily addressable. The way forward is twofold.

— Obtain ground-based spectra in Z, J, H, K, L bands to record the exoplanetary signal in the NIR–MIR spectral region [68]. While water vapour is clearly the most difficult molecule to be observed from the ground, repeated observations can be used to break the degeneracy between exoplanet and telluric signals, as was done in the case of methane [40].
— Adopt new and independent data analysis techniques to break the noise-result degeneracy more efficiently and recover the original results [69]. Statistical techniques used in cosmology and communication

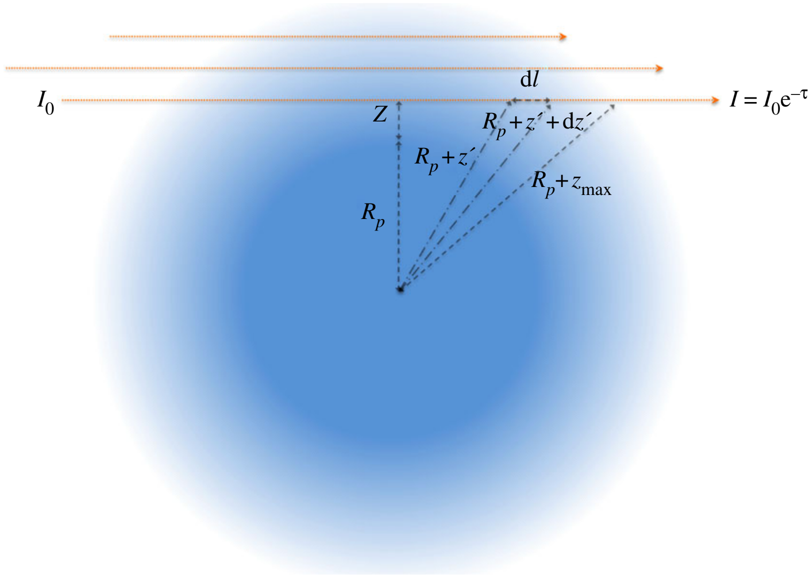

Figure 1. Geometry of a transit observation: the stellar photons are filtered through the planetary atmosphere. (Online version in colour.)

science to optimize the extraction of a weak signal from a noisy background find more and more applicability in the analysis of exoplanetary signals [70–72].

Looking to the longer term, a proposal was made to the European Space Agency (ESA) for a dedicated space mission to observe the atmospheres of tens of known exoplanets over a broad wavelength range: from 0.4 to 16 μm. EChO, the Exoplanet Characterisation Observatory, is one of the four M3 mission candidates currently being assessed by ESA, for a possible launch in 2022.[1] EChO will provide low- to mid-resolution, simultaneous multi-wavelength spectroscopic observations on a stable platform that will allow very long exposures: the design of the whole detection chain and satellite will be dedicated to achieve a high degree of photometric stability and repeatability. EChO's design will be optimized to retrieve the molecular composition and thermal structure of both hot gaseous planets and terrestrial habitable ones [73].

3. The models

Here, we detail our model that calculates the transmission spectrum of an exoplanet atmosphere during primary transit. As shown in figure 1, the stellar radiation traversing the planet is weakened by its interaction with the atmospheric

[1]See http://sci.esa.int/science-e/www/area/index.cfm?fareaid=124.

matter during a transit. Under these circumstances, the Beer–Bouguer–Lambert law gives

$$I(\lambda, z) = I_0\, \mathrm{e}^{-\tau(\lambda,z)}; \quad \tau(\lambda, z) = \sum_i \tau_i(\lambda, z), \tag{3.1}$$

where I_0 is the intensity of the stellar radiation impinging on the top of the planetary atmosphere, I is the intensity of the stellar radiation filtered through the planetary atmosphere, τ is the optical path, i the type of molecule, λ the wavelength and z a given height above $R_p = z(p_0)$. We assume that at some radius, R_p, the planetary atmosphere is completely opaque for all λ. For a terrestrial (rocky) planet, this usually happens at the planetary surface. In contrast, for a gas giant, p_0 should be chosen between approximately 1 and 10 bar, depending on the transparency of the atmosphere. We then calculate the opacity of the atmosphere as a function of λ.

To convert the atmospheric pressure, p, into height, z, we assume hydrostatic equilibrium and ideal gas law are acceptable approximations:

$$\frac{p}{\rho} = kT; \quad \mathrm{d}p = \mu\rho g\, \mathrm{d}z; \quad \rho = \frac{N}{V}, \tag{3.2}$$

where μ is the mean molecular mass, T the temperature, g the gravity, ρ the molecular density and k the Boltzmann constant. At an altitude z, the optical path for a molecule i can be calculated [74]:

$$\tau_i(\lambda, z) = 2\int_0^{\ell(z)} \rho(z')\chi_i(z')\sigma_i(\lambda, T)\, \mathrm{d}\ell, \tag{3.3}$$

where σ_i is the absorption coefficient for the ith molecule at wavelength λ and $\chi_i(z)$ is the mixing ratio for ith molecule at altitude z.

The path traversed by the stellar photons can be easily calculated, the geometry is shown in figure 1:

$$\mathrm{d}\ell = \sqrt{(R_p + z' + \mathrm{d}z')^2 - (R_p + z)^2} - \sqrt{(R_p + z')^2 - (R_p + z)^2} \tag{3.4}$$

and

$$\ell(z) = \int \mathrm{d}\ell = \sqrt{(R_p + z_{\max})^2 - (R_p + z)^2}. \tag{3.5}$$

Finally, the transit depth as a function of λ can be estimated as

$$\kappa(\lambda) = \frac{R_p^2 + 2\int_0^{z_{\max}} (R_p + z)(1 - \mathrm{e}^{-\tau(z,\lambda)})\, \mathrm{d}z}{R_*^2}, \tag{3.6}$$

where R_* is the stellar radius.

4. Comparison with other models

(a) *Linelists*

It has long been recognized that a detailed, temperature-dependent opacity of water vapour is important for models of hot bodies ranging from rocket plumes to M-dwarf stars. The earliest attempt to solve this problem was the experiments

Table 1. Summary of calculated water linelists. Statistics for the latest edition of the empirically derived, room-temperature, HITRAN database are given for comparison.

name	reference	10^6 lines	nuclear motion	potential energy surface
HITEMP91	Wattson & Rothman [48]	0.15	variational, finite basis	empirical
MT	Allard *et al.* [82]	6.2	variational, finite basis	empirical
VTP1	Viti *et al.* [83]	0.23	discrete variable representation	empirical
PS or AMES	Partridge & Schwenke [77]	300	variational, finite basis	tuned *ab initio*
SCAN	Jorgensen *et al.* [80]	3000	approximate	*ab initio*
BT2	Barber *et al.* [47]	504	discrete variable representation	tuned *ab initio*
HITRAN	Barber *et al.* [84]	0.069	empirical	not applicable

of Ludwig [75]. This opacity was used for some time but was well known to over-absorb. This problem was caused by the resolution of the experiments that leads to a quasi-continuous opacity function instead of a highly structured one with gaps through which photons can escape; see Schryber *et al.* [76].

Modern attempts to solve the water opacity problem have been based on the use of calculated linelists. The most important of these are summarized in table 1. The AMES [77] and BT2 [47] are spectroscopically very much more accurate than the other theoretical attempts to characterize the rotation–vibration spectrum of hot water. These linelists give rather similar results when used for modelling hot objects (e.g. Allard [78]), although BT2 is somewhat more complete. The HITEMP91, MT and VTP1 linelists are all too incomplete to be completely reliable; although we note that the recent release of HITEMP [79] is based on BT2 rather than the earlier variational calculations of Wattson & Rothman [48]. The SCAN linelist [80] has very many more transitions than the other lists; however, this linelist is far from spectroscopic accuracy and is well known to significantly overestimate the amount of absorption [81].

Included in table 1 is also a summary of water data included in the 2008 edition of the HITRAN [84]. This database differs from the other linelists as (i) it is largely based on laboratory measurements, (ii) it is aimed at room temperature rather than hot applications and (iii) it contains data on isotopically substituted water. In this context, we note that there is also a BT2-like linelist for HDO called VTT [85]. Schryber *et al.* [76] have already demonstrated how HITRAN lacks the necessary lines to model the absorption by hot water.

Figure 2 shows the calculated water absorption coefficients with BT2 as a function of T illustrating the strong temperature dependence of the opacity.

(*b*) *Radiative models*

Our IR transmission model described in Tinetti *et al.* [45] and detailed in the previous section is based on very similar assumptions to the models of Seager & Sasselov [86] and Brown *et al.* [87]. Clearly, the absorption coefficients at high temperature are today known with higher level of accuracy than they were in

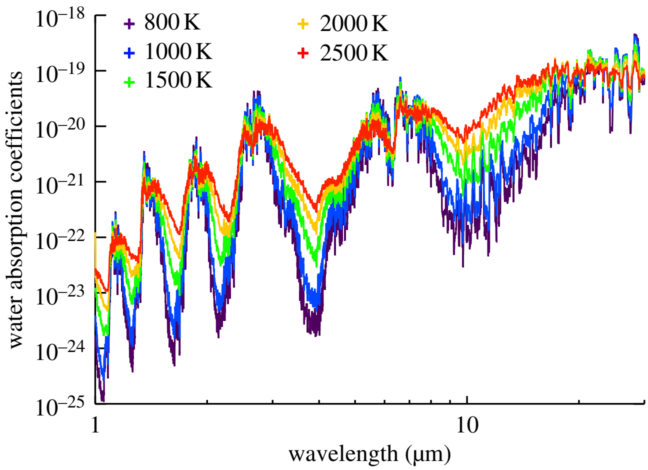

Figure 2. Water absorption coefficients (cm^2 per molecule) calculated with BT2 as a function of temperature. The effect of temperature is dramatic. (Online version in colour.)

2001 or even 2007. Our transmission model was used to fit the HD 189733b transit spectrum recorded with NICMOS [18]. Madhusudhan & Seager obtained consistent results when they analysed the same dataset with their model, which uses the AMES molecular line data of Partridge & Schwenke [77].

Shabram *et al.* [88] have recently cast doubts on the correctness and validity of our transmission model, on the basis they could not reproduce the observations in the literature that our model is able to capture. To make their point, they used an analytical relation by Lecavelier Des Etangs *et al.* [89] to estimate the planetary radius as a function of wavelength. For this purpose, they assume an isothermal temperature structure, a constant gravitational acceleration with height and an opacity cross section that varies as a power law:

$$\sigma = \sigma_0 \left(\frac{\lambda}{\lambda_0}\right)^{\alpha}. \tag{4.1}$$

With these hypotheses, according to Lecavelier Des Etangs *et al.* [89], the radius of the planet can be calculated as

$$\frac{\mathrm{d}R_p}{\mathrm{d}\ln\lambda} = \alpha\frac{kT}{\mu g} = \alpha H. \tag{4.2}$$

Shabram *et al.* [88] consider only a single temperature, 1500 K, and compare absorption coefficients calculated at 1500 K to a planetary radius assuming a single temperature; in this way, they eliminate temperature effects. This approach masks the significant variation of absorption coefficients with wavelength.

5. Results

We have run a number of models to help assess the role of water vapour in exoplanetary atmospheres. The results of these models are summarized in figures 2–5.

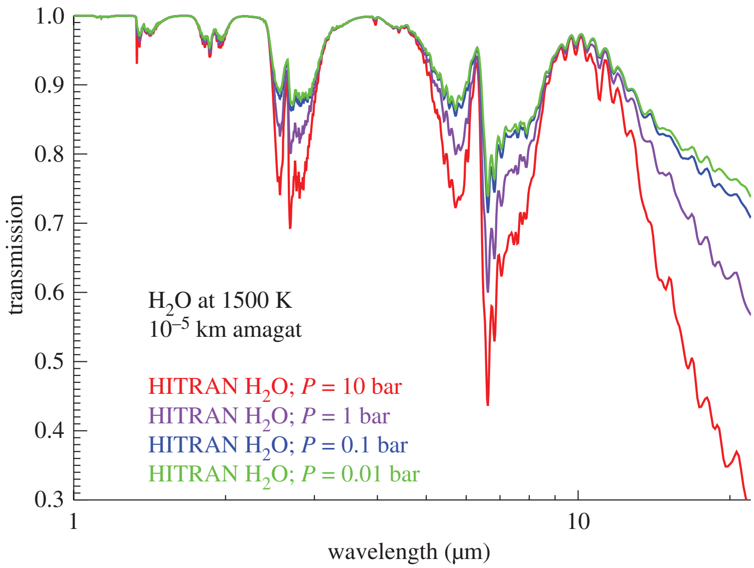

Figure 3. Transmission of stellar flux through a water vapour-containing planetary atmosphere as a function of the pressure of H_2 at a notional fixed temperature of 1500 K. (Online version in colour.)

Figure 2 shows the BT2 water absorption coefficients as a function of temperature: they clearly do not follow a power law (equation (4.1)) as a function of λ as proposed by Shabram *et al.* [88]. The only opacity following a power law as a function of λ is the Rayleigh scattering, behaving as $\sim 1/\lambda^4$. In contrast the water cross section depends not only on temperature but also on pressure, figure 3, and the curve of growth of spectral lines. Therefore, this simple approximation does not necessarily apply, even for small regions of the water spectrum at a single given temperature, as assumed by Shabram *et al.* [88]. As a consequence equation (4.2) should not be used to calculate the transmission spectrum of an exoplanet, as it is not physically meaningful for molecular opacities.

Figure 3 is an attempt to estimate the effect of pressure on the absorption spectrum of water at elevated temperatures. These models used HITRAN 2008, since this database unlike the other linelists discussed above contains pressure broadening parameters. Models were performed at a single temperature, 1500 K, but for a range of pressures for constant water column of 10^{-5} km amagat. They clearly show sensitivity to pressure effects particularly at long wavelengths where the majority of transitions are due to rotational excitation. HITRAN pressure parameters are actually for air (and self) broadening. There have been recent attempts to extend these parameters to the higher levels encountered in hot spectra [90,91], but work on line-broadening by H_2 has largely concentrated on low-temperature [92,93] and room temperature applications [94,95]. There appears to be a clear need to extend this work to deal with high temperature collisional broadening by hydrogen molecules. In the case of water, it would appear that broadening of the pure rotational transitions is of particular importance.

We have investigated the fraction of the stellar IR flux occulted by the planet during the primary transit as a function of wavelength as predicted by our simulations. For this, we simulated a planet similar to HD 209458b with an

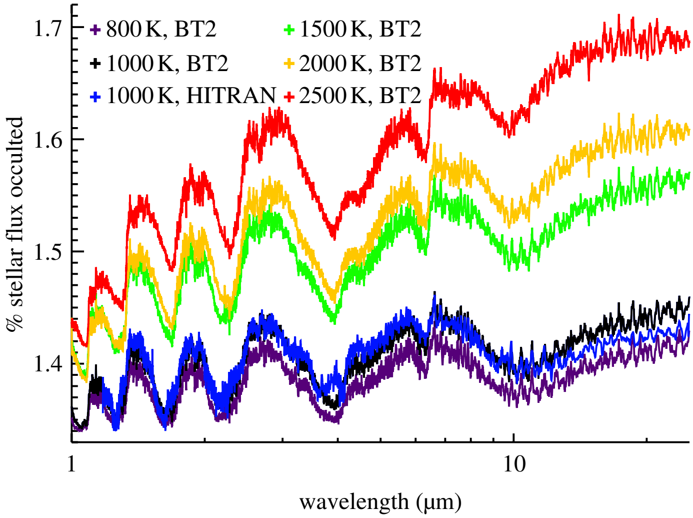

Figure 4. Fraction of the stellar flux occulted by a planet during the primary transit (in %) as a function of wavelength (between 1 and 25 μm) and as a function of changing atmospheric temperature for a fixed water vapour mixing ratio of 10^{-5}. (Online version in colour.)

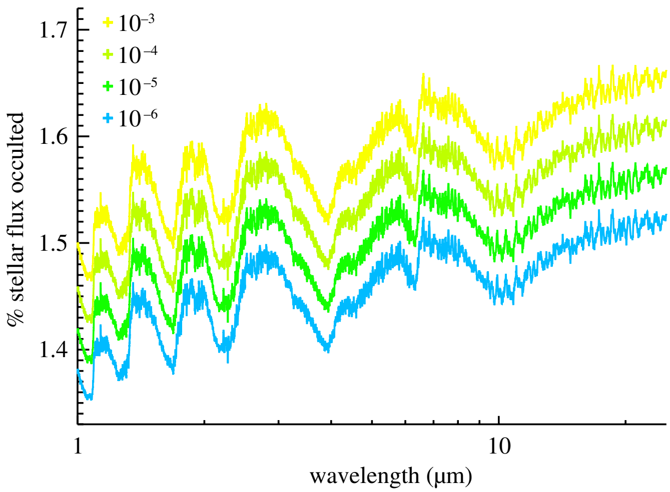

Figure 5. Fraction of the stellar flux occulted by a planet during the primary transit (in %) as a function of wavelength (between 1 and 25 μm) for change of water mixing ratio for a fixed temperature of 1500 K. (Online version in colour.)

atmosphere made of hydrogen and with water vapour as a minor constituent. The unknown planetary radius at 10 bar was fixed for all the cases presented here. Figure 4 gives results computed for a fixed water vapour mixing ratio at 10^{-5} and changing atmospheric temperature, which we assumed here to be isothermal. When HITRAN 2008 is used to estimate the absorption coefficients at 1000 K, we obtained almost overlapping results to BT2 in terms of 'spectral shape' at wavelengths shorter than 10 μm, but the mixing ratio needed for water vapour is higher than that needed with BT2. At longer wavelengths, the spectrum calculated with HITRAN 2008 underestimates the water rotational absorption owing to the lack of rotational transitions between both highly excited rotational states within the ground vibrational state and within 'hot' vibrational states. Figure 5 shows the effect of increasing the mixing ratio for a fixed temperature of 1500 K.

6. Conclusions

Water is thought to be one of the most important species in exoplanetary atmospheres. Space-based transit observations have given strong indications that water is indeed present in significant quantities in the hot, gas giant exoplanets for which such observations have been possible. However, observations are presently strongly hampered by the difficulty of observing astronomical water spectra from the ground and spaceborne telescopes. Despite our confidence in the positive detections of water, some of which have been confirmed by both independent observations and models, a number of uncertainties remain. Among those, current and foreseeable future observations will not allow us to constrain accurately the water vapour abundances, given the level of degeneracy embedded in transit observations. Simultaneous broad band coverage, good signal-to-noise ratio and spectral resolution are needed to tackle such a task consistently; in other words, a dedicated space mission—such as the ESA-EChO—is the obvious next step.

We agree with Freedman *et al.* [96] that the extensive theoretical linelists AMES [77] and BT2 [47] give similar results; however, these linelists do not make any allowance for pressure broadening of the transitions. There is a need for data on high temperature broadening of water lines by molecular hydrogen. This is necessary as the assumptions underlying the calculation of these absorption coefficients lead to a range of models with significantly different results.

G.T. is a Royal Society University Research Fellow. J.T. thanks the European Research Council for funding under ERC Advanced Investigator Project 26721. I.W. PhD studentship is funded by STFC.

References

1 Mayor, M., & Queloz, D. 1995 A Jupitor-mass companion to a solar-type star. *Nature* **378**, 355–359. (doi:10.1038/378355a0)

2 Schneider, J. 2011 The extrasolar planets encyclopaedia. See http://exoplanet.eu/catalog.php.

3 Borucki, W. J. *et al.* 2011 Characteristics of planetary candidates observed by *Kepler*. II. Analysis of the first four months of data. *Astrophys. J.* **736**, 19. (doi:10.1088/0004-637X/736/1/19)

4 Tsiganis, K., Gomes, R., Morbidelli, A. & Levison, H. F. 2005 Origin of the orbital architecture of the giant planets of the Solar System. *Nature* **435**, 459–461. (doi:10.1038/nature03539)

5 Howard, A. W. *et al.* 2011 Planet occurrence within 0.25 AU of solar-type stars from Kepler. (http://arxiv.org/abs/1103.2541)

6 Mayor, M. *et al.* 2011 The HARPS search for southern extra-solar planets XXXIV. Occurrence, mass distribution and orbital properties of super-Earths and Neptune-mass planets. (http://arxiv.org/abs/1109.2497)

7 Charbonneau, D., Brown, T. M., Noyes, R. W. & Gilliland, R. L. 2002 Detection of an extrasolar planet atmosphere. *Astrophys. J.* **568**, 377–384. (doi:10.1086/338770)

8 Charbonneau, D. *et al.* 2005 Detection of thermal emission from an extrasolar planet. *Astrophys. J.* **626**, 523–529. (doi:10.1086/429991)
9 Deming, D., Seager, S., Richardson, L. J. & Harrington, J. 2005 Infrared radiation from an extrasolar planet. *Nature* **434**, 740–743. (doi:10.1038/nature03507)
10 Harrington, J., Hansen, B. M., Luszcz, S. H., Seager, S., Deming, D., Menou, K., Cho, J. Y.-K. & Richardson, L. J. 2006 The phase-dependent infrared brightness of the extrasolar planet upsilon Andromedae b. *Science* **314**, 623–626. (doi:10.1126/science.1133904)
11 Knutson, H. A., Charbonneau, D., Allen, L. E., Fortney, J. J., Agol, E., Cowan, N. B., Showman, A. P., Cooper, C. S. & Megeath, S. T. 2007 A map of the day–night contrast of the extrasolar planet HD 189733b. *Nature* **447**, 183–186. (doi:10.1038/nature05782)
12 Snellen, I. A. G., de Mooij, E. J. W. & Albrecht, S. 2009 The changing phases of extrasolar planet CoRoT-1b. *Nature* **459**, 543–545. (doi:10.1038/nature08045)
13 Borucki, W. J. *et al.* 2009 Kepler's optical phase curve of the exoplanet HAT-P-7b. *Science* **325**, 709. (doi:10.1126/science.1178312)
14 Crossfield, I. J. M., Hansen, B. M. S., Harrington, J., Cho, J., Deming, D., Menou, K. & Seager, S. 2010 A new 24 micron phase curve for υ Andromedae b. *Astrophys. J.* **723**, 1436–1446. (doi:10.1088/0004-637X/723/2/1436)
15 Knutson, H. A., Charbonneau, D., Noyes, R. W., Brown, T. M. & Gilliland, R. L. 2007 Using stellar limb-darkening to refine the properties of HD 209458b. *Astrophys. J.* **655**, 564–575. (doi:10.1086/510111)
16 Tinetti, G. *et al.* 2007 Water vapour in the atmosphere of a transiting extrasolar planet. *Nature* **448**, 169–171. (doi:10.1038/nature06002)
17 Tinetti, G., Deroo, P., Swain, M. R., Griffith, C. A., Vasisht, G., Brown, L. R., Burke, C. & McCullough, P. 2010 Probing the terminator region atmosphere of the hot-Jupiter XO-1b with transmission spectroscopy. *Astrophys. J.* **712**, L139–L142. (doi:10.1088/2041-8205/712/2/L139)
18 Swain, M. R., Vasisht, G. & Tinetti, G. 2008 The presence of methane in the atmosphere of an extrasolar planet. *Nature* **452**, 329–331. (doi:10.1038/nature06823)
19 Swain, M. R. *et al.* 2009 Water, methane, and carbon dioxide present in the dayside spectrum of the exoplanet HD 209458b. *Astrophys. J.* **704**, 1616–1621. (doi:10.1088/0004-637X/704/2/1616)
20 Swain, M. R., Vasisht, G., Tinetti, G., Bouwman, J., Chen, P., Yung, Y., Deming, D. & Deroo, P. 2009 Molecular signatures in the near-infrared dayside spectrum of HD 189733b. *Astrophys. J.* **690**, L114–L117. (doi:10.1088/0004-637X/690/2/L114)
21 Grillmair, C. J. 2008 Strong water absorption in the dayside emission spectrum of the planet HD189733b. *Nature* **456**, 767–769. (doi:10.1038/nature07574)
22 Rowe, J. F. *et al.* 2006 An upper limit on the albedo of HD 209458b: direct imaging photometry with the MOST satellite. *Astrophys. J.* **646**, 1241–1251. (doi:10.1086/504252)
23 Vidal-Madjar, A., Lecavelier des Etangs, A., Désert, J.-M., Ballester, G. E., Ferlet, R., Hébrard, G. & Mayor, M. 2003 An extended upper atmosphere around the extrasolar planet HD209458b. *Nature* **422**, 143–146. (doi:10.1038/nature01448)
24 Linsky, J. L., Yang, H., France, K., Froning, C. S., Green, J. C., Stocke, J. T. & Osterman, S. N. 2010 Observations of mass loss from the transiting exoplanet HD 209458b. *Astrophys. J.* **717**, 1291–1299. (doi:10.1088/0004-637X/717/2/1291)
25 Stevenson, K. B. *et al.* 2010 Possible thermochemical disequilibrium in the atmosphere of the exoplanet GJ 436b. *Nature* **464**, 1161–1164. (doi:10.1038/nature09013)
26 Beaulieu, J.-P. *et al.* 2011 Methane in the atmosphere of the transiting hot Neptune GJ436B? *Astrophys. J.* **731**, 16. (doi:10.1088/0004-637X/731/1/16)
27 Richardson, L. J., Deming, D. & Seager, S. 2003 Infrared observations during the secondary eclipse of HD 209458b. II. Strong limits on the infrared spectrum near 2.2 μm. *Astrophys. J.* **597**, 581–589. (doi:10.1086/378390)
28 Barnes, J. R., Barman, T. S., Prato, L., Segransan, D., Jones, H. R. A., Leigh, C. J., Collier Cameron, A. & Pinfield, D. J. 2007 Limits on the 2.2-μm contrast ratio of the close-orbiting planet HD 189733b. *Mon. Not. R. Astron. Soc.* **382**, 473–480. (doi:10.1111/j.1365-2966.2007.12394.x)
29 Barnes, J. R., Barman, T. S., Jones, H. R. A., Leigh, C. J., Collier Cameron, A., Barber, R. J. & Pinfield, D. J. 2008 HD179949b: a close orbiting extrasolar giant planet with a stratosphere? *Mon. Not. R. Astron. Soc.* **390**, 1258–1266. (doi:10.1111/j.1365-2966.2008.13831.x)

30 Barnes, J. R. *et al.* 2010 A search for molecules in the atmosphere of HD 189733b. *Mon. Not. R. Astron. Soc.* **401**, 445–454. (doi:10.1111/j.1365-2966.2009.15654.x)

31 Mandell, A. M., Drake Deming, L., Blake, G. A., Knutson, H. A., Mumma, M. J., Villanueva G. L. & Salyk, C. 2011 Non-detection of L-band line emission from the exoplanet HD189733b. *Astrophys. J.* **728**, 18. (doi:10.1088/0004-637X/728/1/18)

32 Redfield, S., Endl, M., Cochran, W. D. & Koesterke, L. 2008 Sodium absorption from the exoplanetary atmosphere of HD 189733b detected in the optical transmission spectrum. *Astrophys. J.* **673**, L87–L90. (doi:10.1086/527475)

33 Snellen, I. A. G., Albrecht, S., de Mooij, E. J. W. & Le Poole, R. S. 2008 Ground-based detection of sodium in the transmission spectrum of exoplanet HD 209458b. *Astron. Astrophys.* **487**, 357–362. (doi:10.1051/0004-6361:200809762)

34 Sing, D. K. *et al.* 2011 Gran Telescopio Canarias OSIRIS transiting exoplanet atmospheric survey: detection of potassium in XO-2b from narrowband spectrophotometry. *Astron. Astrophys.* **527**, A73. (doi:10.1051/0004-6361/201015579)

35 Colon, K. D., Ford, E. B., Redfield, S., Fortney, J. J., Shabram, M., Deeg, H. J. & Mahadevan, S. 2012 Probing potassium in the atmosphere of HD 80606b with tunable filter transit spectrophotometry from the Gran Telescopio Canarias. *Mon. Not. R. Astron. Soc.* **419**, 2233–2250. (doi:10.1111/j.1365-2966.2011.19878.x)

36 Charbonneau, D. *et al.* 2009 A super-Earth transiting a nearby low-mass star. *Nature* **462**, 891–894. (doi:10.1038/nature08679)

37 Bean, J. L., Miller-Ricci Kempton, E. & Homeier, D. 2010 A ground-based transmission spectrum of the super-Earth exoplanet GJ 1214b. *Nature* **468**, 669–672. (doi:10.1038/nature09596)

38 Snellen, I. A. G., de Kok, R. J., de Mooij, E. J. W. & Albrecht, S. 2010 The orbital motion, absolute mass and high-altitude winds of exoplanet HD209458b. *Nature* **465**, 1049–1051. (doi:10.1038/nature09111)

39 Swain, M. R. *et al.* 2010 A ground-based near-infrared emission spectrum of the exoplanet HD189733b. *Nature* **463**, 637–639. (doi:10.1038/nature08775)

40 Waldmann, I. P., Tinetti, G., Drossart, P., Griffith, C. A., Swain, M. R. & Deroo, P. 2012 Ground-based NIR emission spectroscopy of HD189733b. *Astrophys. J.* **744**, 35. (doi:10.1088/0004-637X/744/1/35)

41 Richardson, L. J., Deming, D., Horning, K., Seager, S. & Harrington, J. 2007 A spectrum of an extrasolar planet. *Nature* **445**, 892–895. (doi:10.1038/nature05636)

42 Grillmair, C. J., Charbonneau, D., Burrows, A., Armus, L., Stauffer, J., Meadows, V., Van Cleve, J. & Levine, D. 2007 A Spitzer spectrum of the exoplanet HD 189733b. *Astrophys. J.* **658**, L115–L118. (doi:10.1086/513741)

43 Swain, M. R., Bouwman, J., Akeson, R. L., Lawler, S. & Beichman, C. A. 2008 The mid-infrared spectrum of the transiting exoplanet HD 209458b. *Astrophys. J.* **674**, 482–497. (doi:10.1086/523832)

44 Barman, T. 2007 Identification of absorption features in an extrasolar planet atmosphere. *Astrophys. J.* **661**, L191–L194. (doi:10.1086/518736)

45 Tinetti, G., Liang, M.-C., Vidal-Madjar, A., Ehrenreich, D., Lecavelier des Etangs, A. & Yung, Y. L. 2007 Infrared transmission spectra for extrasolar giant planets. *Astrophys. J.* **654**, L99–L102. (doi:10.1086/510716)

46 Beaulieu, J. P., Carey, S., Ribas, I. & Tinetti, G. 2008 Primary transit of the planet HD 189733b at 3.6 and 5.8 µm. *Astrophys. J.* **677**, 1343–1347. (doi:10.1086/527045)

47 Barber, R. J., Tennyson, J., Harris, G. J. & Tolchenov, R. N. 2006 A high accuracy computed water line list. *Mon. Not. R. Astron. Soc.* **368**, 1087–1094. (doi:10.1111/j.1365-2966.2006.10184.x)

48 Wattson, R. B. & Rothman, L. S. 1992 Direct numerical diagonalization—wave of the future. *J. Quant. Spectrosc. Radiat. Transf.* **48**, 763–780. (doi:10.1016/0022-4073(92)90140-Y)

49 Charbonneau, D., Knutson, H. A., Barman, T., Allen L. E., Mayor, M., Megeath, S. T., Queloz, D. & Udry, S. 2008 The broadband infrared emission spectrum of the exoplanet HD 189733b. *Astrophys. J.* **686**, 1341–1348. (doi:10.1086/591635)

50 Knutson, H. A., Charbonneau, D., Allen, L. E., Burrows, A. & Megeath, S. T. 2008 The 3.6–8.0 μm broadband emission spectrum of HD 209458b: evidence for an atmospheric temperature inversion. *Astrophys. J.* **673**, 526–531. (doi:10.1086/523894)

51 Beaulieu, J. P. *et al.* 2010 Water in the atmosphere of HD 209458b from 3.6–8 μm IRAC photometric observations in primary transit. *Mon. Not. R. Astron. Soc.* **409**, 963–974. (doi:10.1111/j.1365-2966.2010.16516.x)

52 Burrows, A., Hubeny, I., Budaj, J., Knutson, H. A. & Charbonneau, D. 2007 Theoretical spectral models of the planet HD 209458b with a thermal inversion and water emission bands. *Astrophys. J.* **668**, L171–L174. (doi:10.1086/522834)

53 Burrows, A., Budaj, J. & Hubeny, I. 2008 Theoretical spectra and light curves of close-in extrasolar giant planets and comparison with data. *Astrophys. J.* **678**, 1436–1457. (doi:10.1086/533518)

54 Burrows, A., Rauscher, E., Spiegel, D. S. & Menou, K. 2010 Photometric and spectral signatures of three-dimensional models of transiting giant exoplanets. *Astrophys. J.* **719**, 341–350. (doi:10.1088/0004-637X/719/1/341)

55 Barman, T. S. 2008 On the presence of water and global circulation in the transiting planet HD 189733b. *Astrophys. J.* **676**, L61–L64. (doi:10.1086/587056)

56 Showman, A. P., Fortney, J. J., Lian, Y., Marley, M. S., Freedman, R. S., Knutson, H. A. & Charbonneau, D. 2009 Atmospheric circulation of hot jupiters: coupled radiative-dynamical general circulation model simulations of HD 189733b and HD 209458b. *Astrophys. J.* **699**, 564–584. (doi:10.1088/0004-637X/699/1/564)

57 Madhusudhan, N. & Seager, S. 2009 A temperature and abundance retrieval method for exoplanet atmospheres. *Astrophys. J.* **707**, 24–39. (doi:10.1088/0004-637X/707/1/24)

58 Pont, F., Knutson, H., Gilliland, R. L., Moutou, C. & Charbonneau, D. 2008 Detection of atmospheric haze on an extrasolar planet: the 0.55–1.05 μm transmission spectrum of HD 189733b with the Hubble Space Telescope. *Mon. Not. R. Astron. Soc.* **385**, 109–118. (doi:10.1111/j.1365-2966.2008.12852.x)

59 Sing, D. K. *et al.* 2011 Hubble Space Telescope transmission spectroscopy of the exoplanet HD 189733b: high-altitude atmospheric haze in the optical and near-ultraviolet with STIS. *Mon. Not. R. Astron. Soc.* **416**, 1443–1455. (doi:10.1111/j.1365-2966.2011.19142.x)

60 Lee *et al.* 2012 Optimal estimation retrievals of the atmospheric structure and composition of HD 189733b from secondary eclipse spectroscopy. *Mon. Not. R. Astronom. Soc.* **420**, 170–182. (doi:10.1111/j.1365-2966.2011.20013.x)

61 Line *et al.* 2012 Information content of exoplanetary transit spectra: an initial look. http://adsabs.harvard.edu/abs/2011arXiv1111.2612L.

62 Tinetti, G. *et al.* 2010 Exploring extrasolar worlds: from gas giants to terrestrial habitable planets. *Faraday Discuss.* **147**, 369–377. (doi:10.1039/c005126h)

63 Désert, J.-M., Lecavelier des Etangs, A., Hébrard, G., Sing, D. K., Ehrenreich, D., Ferlet, R. & Vidal-Madjar, A. 2009 Search for carbon monoxide in the atmosphere of the transiting exoplanet HD 189733b. *Astrophys. J.* **699**, 478–485. (doi:10.1088/0004-637X/699/1/478)

64 Sing, D. K., Désert, J.-M., Lecavelier Des Etangs, A., Ballester, G. E., Vidal-Madjar, A., Parmentier, V., Hebrard, G. & Henry, G. W. 2009 Transit spectrophotometry of the exoplanet HD 189733b. I. Searching for water but finding haze with HST NICMOS. *Astron. Astrophys.* **505**, 891–899. (doi:10.1051/0004-6361/200912776)

65 Gibson, N. P., Pont, F. & Aigrain, S. 2011 A new look at NICMOS transmission spectroscopy of HD 189733, GJ-436 and XO-1: no conclusive evidence for molecular features. *Mon. Not. R. Astron. Soc.* **411**, 2199–2213. (doi:10.1111/j.1365-2966.2010.17837.x)

66 Swain, M., Deroo, P. & Vasisht, G. 2011 NICMOS spectroscopy of HD 189733b. *Proc. Int. Astron. Union* **6** (Symp. S276), 148–153. (doi:10.1017/S1743921311020096)

67 Gibson *et al.* 2012 A Gaussian process framework for modelling instrumental systematics: application to transmission spectroscopy. *Mon. Not. R. Astron. Soc.* **419**, 2683–2694. (doi:10.1111/j.1365-2966.2011.19915.x)

68 Danielski, C., Deroo, P., Waldmann, I. P., Tinetti, G. & Swain, M. Submitted. 1.4-2.4 micron ground-based transmission spectra of the hot Jupiter HD-189733b, *Astrophys. J.*

69 Waldmann, I. P. 2011 Of 'Cocktail parties' and exoplanets. *Astrophys. J.* **747**, 12. (doi:10.1088/0004-637X/747/1/12)
70 Carter, J. A. & Winn, J. N. 2009 Parameter estimation from time-series data with correlated errors: a wavelet-based method and its application to transit light curves. *Astrophys. J.* **704**, 51–67. (doi:10.1088/0004-637X/704/1/51)
71 Gregory, P. C. 2011 Bayesian exoplanet tests of a new method for MCMC sampling in highly correlated model parameter spaces. *Mon. Not. R. Astron. Soc.* **410**, 94–110. (doi:10.1111/j.1365-2966.2010.17428.x)
72 Feroz, F., Balan, S. T. & Hobson, M. P. 2011 Bayesian evidence for two companions orbiting HIP 5158. *Mon. Not. R. Astron. Soc.* **416**, L104–L108. (doi:10.1111/j.1745-3933.2011.01109.x)
73 Tinetti, G. *et al.* In press. Exoplanet characterisation observatory. *Exp. Astron.*
74 Liou, K. N. 1980 *An introduction to atmospheric radiation.* New York, NY: Academic Press.
75 Ludwig, C. B. 1971 Measurements of curves-of-growth of hot water vapor. *Appl. Opt.* **10**, 1057–1073. (doi:10.1364/AO.10.001057)
76 Schryber, J. H., Miller, S. & Tennyson, J. 1995 Computed infrared absorption properties of hot water vapour. *J. Quant. Spectrosc. Radiat. Transf.* **53**, 373–380. (doi:10.1016/0022-4073(95)90013-6)
77 Partridge, H. & Schwenke, D. W. 1997 The determination of an accurate isotope dependent potential energy surface for water from extensive ab initio calculations and experimental data. *J. Chem. Phys.* **106**, 4618–4639. (doi:10.1063/1.473987)
78 Allard, F., Homeier, D. & Freytag, B. 2012 Models of very-low-mass stars, brown dwarfs and exoplanets. *Phil. Trans. R. Soc. A* **370**, 2765–2777. (doi:10.1098/rsta.2011.0269)
79 Rothman, L. S., Gordon, I. E., Barber, R. J., Dothe, H., Gamache, R. R., Goldman, A., Perevalov, V. I., Tashkun, S. A. & Tennyson, J. 2010 HITEMP, the high-temperature molecular spectroscopic database. *J. Quant. Spectrosc. Radiat. Transf.* **111**, 2139–2150. (doi:10.1016/j.jqsrt.2010.05.001)
80 Jorgensen, U. G., Jensen, P., Sorensen, G. O. & Aringer, B. 2001 H_2O in stellar atmospheres. *Astron. Astrophys.* **372**, 249–259. (doi:10.1051/0004-6361:20010285)
81 Jones, H. R. A., Pavlenko, Y., Viti, S. & Tennyson, J. 2002 Spectral analysis of water vapour in cool dwarf stars. *Mon. Not. R. Astron. Soc.* **330**, 675–684. (doi:10.1046/j.1365-8711.2002.05090.x)
82 Allard, F., Hauschildt, P. H., Miller, S. & Tennyson, J. 1994 The influence of H_2O line blanketing on the spectra of cool dwarf stars. *Astrophys. J.* **426**, L39–L41. (doi:10.1086/187334)
83 Viti, S., Tennyson, J. & Polyansky, O. L. 1997 A spectroscopic linelist for hot water. *Mon. Not. R. Astron. Soc.* **287**, 79–86.
84 Rothman, L. *et al.* 2009 The *HITRAN* 2008 molecular spectroscopic database. *J. Quant. Spectrosc. Radiat. Transf.* **110**, 533–572. (doi:10.1016/j.jqsrt.2009.02.013)
85 Voronin, B. A., Tennyson, J., Tolchenov, R. N., Lugovskoy, A. A. & Yurchenko, S. 2010 A high accuracy computed line list for the HDO molecule. *Mon. Not. R. Astron. Soc.* **402**, 492–496. (doi:10.1111/j.1365-2966.2009.15904.x)
86 Seager, S. & Sasselov, D. D. 2000 Theoretical transmission spectra during extrasolar giant planet transits. *Astrophys. J.* **537**, 916–921. (doi:10.1086/309088)
87 Brown, T. M., Charbonneau, D., Gilliland, R. L., Noyes, R. W. & Burrows, A. 2001 Hubble Space Telescope time-series photometry of the transiting planet of HD 209458. *Astrophys. J.* **552**, 699–709. (doi:10.1086/320580)
88 Shabram, M., Fortney, J. J., Greene, T. P. & Freedman, R. S. 2011 Transmission spectra of transiting planet atmospheres: model validation and simulations of the hot Neptune GJ 436b for the James Webb space telescope. *Astrophys. J.* **727**, 65. (doi:10.1088/0004-637X/727/2/65)
89 Lecavelier Des Etangs, A., Pont, F., Vidal-Madjar, A. & Sing, D. 2008 Rayleigh scattering in the transit spectrum of HD 189733b. *Astron. Astrophys.* **481**, L83–L86. (doi:10.1051/0004-6361:200809388)
90 Voronin, B. A., Lavrentyeva, N. N., Mishina, T. P., Chesnokova, T., Barber, M. J. & Tennyson, J. 2010 Estimate of the $J'J''$ dependence of water vapor line broadening parameters. *J. Quant. Spectrosc. Radiat. Transf.* **111**, 2308–2314. (doi:10.1016/j.jqsrt.2010.05.015)

91 Ma, Q., Tipping, R. H. & Lavrentieva, N. 2011 Pair identity and smooth variation rules applicable for the spectroscopic parameters of H_2O transitions involving high J states. *Mol. Phys.* **109**, 1925–1941. (doi:10.1080/00268976.2011.599343)

92 Dick, M. J., Drouin, B. J. & Pearson, J. C. 2009 A collisional cooling investigation of the pressure broadening of the $1_{10} \leftarrow 1_{01}$ transition of water from 17 to 200 K. *J. Quant. Spectrosc. Radiat. Transf.* **110**, 619–627. (doi:10.1016/j.jqsrt.2008.11.012)

93 Wiesenfeld, L. & Faure, A. 2010 *Ab initio* computation of the broadening of water rotational lines by molecular hydrogen. *Phys. Rev. A* **82**, 040702. (doi:10.1103/PhysRevA.82.040702)

94 Brown, L. R. & Plymate, C. 1996 H_2-broadened $H_2^{16}O$ in four infrared bands between 55 and 4045 cm^{-1}. *J. Quant. Spectrosc. Radiat. Transf.* **56**, 263–282. (doi:10.1016/0022-4073(95)00191-3)

95 Gamache, R. R., Lynch, R. & Neshyba, S. P. 1998 New developments in the theory of pressure-broadening and pressure-shifting of spectral lines of H_2O: the complex Robert-Bonamy formalism. *J. Quant. Spectrosc. Radiat. Transf.* **59**, 319–335. (doi:10.1016/S0022-4073(97)00123-4)

96 Freedman, R. S., Marley, M. S. & Lodders, K. 2008 Line and mean opacities for ultracool dwarfs and extrasolar planets. *Astrophys. J. Suppl.* **174**, 504. (doi:10.1086/521793)