Measuring the D/H Ratios of Exoplanets and Brown Dwarfs

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Abstract

The relative abundance of deuterium and hydrogen is a potent tracer of planet formation and evolution. Jupiter and Saturn have protosolar atmospheric D/H ratios, a relic of substantial gas accretion from the nebula, while the atmospheres of Neptune and Uranus are enhanced in D by accretion of ices into their envelopes. For terrestrial planets, D/H ratios are used to determine the mechanisms of volatile delivery and subsequent atmosphere loss over the lifetime of the planet. Planets and brown dwarfs more massive than ~13 M_J quickly fuse their initial D reservoir. Here, we simulate spectra for giant exoplanets and brown dwarfs (2 M_Neptune to ~10 M_Jupiter) from T_{eff} = 200–1800 K including both CH_3D and HDO to determine the observability of these dominant deuterium isotopologues in mid-infrared thermal emission spectra. Colder objects have stronger molecular features in their spectra, due to the temperature dependence of molecular cross sections. CH_3D is easier to observe than HDO at all temperatures considered, due to the strength of its absorption bands and locations of features at wavelengths with few other strong absorption features. We predict that for nearby cool brown dwarfs, the CH_3D abundance can be measured at high signal to noise with the James Webb Space Telescope (JWST); for objects from 200 to 800 K closer than 10 pc, a protosolar D/H ratio would be readily observable in 2.5 hr. Moderately young Jupiter-mass planets (100–300 Myr) and young Neptunes (10 Myr) may be discovered with JWST and provide the best targets for detecting deuterium on an exoplanet in the coming decade. Future telescope designs should consider the importance of isotopes for understanding the formation and evolution of planetary atmospheres.

Key words: brown dwarfs – planets and satellites: atmospheres – planets and satellites: gaseous planets

1. Introduction

With current instruments, it is possible to detect molecules and elements in exoplanet and brown dwarf atmospheres (e.g., Charbonneau et al. 2002; Kirkpatrick 2005; Kreidberg et al. 2014). The atmospheric enrichment and ratios of elemental abundances inform us about how an object formed: the atmospheres of brown dwarfs that collapse directly out of a molecular cloud are predicted to form with the same elemental abundances as more massive stars forming in that cloud, while planets that form in a disk via core accretion and gas/planetesimal accretion will have abundance patterns that reflect the material available at their locations in the disk (Öberg et al. 2011). For example, planets that form beyond the water ice line will accrete both gas and water-rich ices into their atmospheres; depending on the ratio of gas to ice accreted, the object would have a supersolar or subsolar metallicity and C/O ratio (Espinosa et al. 2017).

In studies of the solar system, a complementary and critical tool for tracing planet formation and evolution is the relative abundances of different isotopes of the same element. One important element is deuterium: the deuterium to hydrogen (D/H) ratio traces a host of different physical processes in an atmosphere, including accretion of solids and gas, atmospheric escape, and deuterium fusion (Owen 1992; Lecluse et al. 1996). In this Letter, in Section 2 we will review these processes to provide motivation for the simulations, in Section 3 we describe the model atmospheres, in Section 4 we examine the possibilities for detection of deuterium in an exoplanet atmosphere, and in Section 5 we discuss the implications of such a detection.

2. D/H Ratios in Planets and Brown Dwarfs

The D/H ratio can vary substantially from the galactic average; measurements for selected objects are shown in Figure 1. The primordial D/H ratio in the universe, set by Big Bang Nucleosynthesis, is (2.8 ± 0.2) × 10^{-5} (Pettini et al. 2008). The Milky Way’s D/H ratio in the gas of the interstellar medium varies along lines of sight by a factor of several, with a mean D/H ratio of (2.0 ± 0.1) × 10^{-5}, typically measured using absorption line spectroscopy of atomic H and D in the far-UV (Prodanović et al. 2010). Ices, both interstellar and within disks, become enhanced in deuterium through several chemical pathways at the cold temperatures (<50 K) present in these environments: gas-phase ion–neutral reactions and grain-surface formation from ionization-generated hydrogen and deuterium atoms from H_2 (Cleeves et al. 2014). D/H ratios in ices are typically measured at millimeter wavelengths using sublimating ice (either from comets or around protostars).
2.1. D/H in Giant Planets Traces Accretion of Solids

Deuterium was first detected outside of the Earth in Jupiter’s atmosphere by Beer et al. (1972). Since then, the deuterium abundances in each of the giant planets’ atmospheres have been measured in the near- infrared using HD rotational features and in the visible and far-infrared using HDD features (Knacke et al. 1982; Kunde et al. 1982; Courtin et al. 1984; de Bergh et al. 1986, 1990; Feuchtgruber et al. 1999; Lellouch et al. 2001, 2010). Jupiter and Saturn have D/H ratios consistent with the protosolar value, though, intriguingly, different from each other as measured using HD features with Cassini Composite Infrared Spectrometer: Jupiter’s D/H is $(2.95 \pm 0.55) \times 10^{-5}$ and Saturn’s is $(2.1 \pm 0.13) \times 10^{-5}$ (Pierel et al. 2017), with Saturn’s lower abundance in conflict with predictions from models (Guillot 1999). Uranus’s and Neptune’s atmospheres are enhanced in deuterium by a factor of $\sim 2.5$.

The classical picture is that the giant planets formed by accretion of ices and gases onto a core of $\sim 10$–15 $M_{\text{Earth}}$ (Stevenson 1982). For Jupiter and Saturn, the relative mass of the core and heavy elements is small compared to the gas accreted, so the D/H ratio is expected to trace the primordial composition of the solar nebula gas. For Uranus and Neptune, more than half of their total masses were accreted as ices; their envelopes are enhanced compared to the solar nebula gas, tracing the relative amount of D-enriched ices that accreted. Assuming that all ices are mainly water, the D/H ratio of the planet is

$$\frac{\text{D/H}}{\text{planet}} = \frac{\text{D/H}_{\text{ices}}(1 - x_{\text{H}_2})}{\text{D/H}_{\text{proto}}x_{\text{H}_2}},$$

where $(\text{D/H})_{\text{planet}}$ is the D/H ratio in the planet, $(\text{D/H})_{\text{ices}}$ is the D/H ratio in ices, $(\text{D/H})_{\text{proto}}$ is the D/H ratio in the protosolar gas, and $x_{\text{H}_2}$ is the volume mixing ratio of H$_2$ in the planet (Lecluse et al. 1996). Much of this ice is incorporated into planetary cores, but models predict that the interior ices exchange deuterium with the hydrogen reservoir (Guillot 1999).

2.2. D/H in Terrestrial Planets Traces Both Volatile Accretion and Atmosphere Loss

Earth, Mars, and Venus have distinct D/H ratios shaped by accretion of volatiles and subsequent atmospheric escape.

The D/H ratios of comets in the Oort Cloud are higher than that of the Earth, suggesting that Earth likely did not accrete the majority of its volatiles from comets (Drake & Righter 2002), but instead from chondrites. However, Hartogh et al. (2011) measured the D/H ratio in a Jupiter-family comet, finding an Earth-like D/H ratio and suggesting that comets and chondrites may both have played a role in volatile delivery.

Venus’s atmosphere is substantially enhanced in deuterium, by a factor of $\sim 100$ above Earth’s (Donahue & Pollack 1983). As Venus went through a runaway greenhouse, its oceans evaporated and H$_2$O photodissociated in its upper atmosphere. The lower mass of H caused it to be more easily lost than D (Donahue & Pollack 1983; Chamberlain & Hunten 1987).

Mars’ D/H ratio is similar to Oort cloud comets. Since Mars does not have plate tectonics that recycle the crust with mantle material, this may reflect a late veneer of accretion from comets rather than a primordial reservoir (Drake 2005).

2.3. D/H in Brown Dwarfs Traces Deuterium Fusion

Brown dwarfs form with approximately protosolar abundances. Those more massive than 20 $M_J$ will efficiently fuse almost all deuterium within 20 Myr; objects under 11 $M_J$ will never fuse their deuterium, retaining primordial abundances (Saumon et al. 1996; Spiegel et al. 2011). The mass at which a brown dwarf will have burned 50% of its deuterium is roughly 13 $M_J$, but depends slightly on initial He fraction, metallicity, and primordial D/H ratio, and is expected to typically range between 12.2 and 13.7 $M_J$ (Spiegel et al. 2011). Most D fusion occurs in the first 100–300 Myr.

3. Methods

3.1. Atmosphere Models

We model the impact of two D-bearing species long-used to detect deuterium in the solar system, deuterated water (HDO) and deuterated methane (CH$_3$D), on the spectra of free-floating planets and brown dwarfs. We consider objects below the deuterium-burning limit ($M < 13 M_J$). We include cloud-free objects with effective temperatures from 200 to 1800 K and log g = 4.0. These $T_{\text{eff}}/g$ pairs cover a broad range of self-luminous free-floating planets. A 4.5 $M_J$ planet will have a log g = 4.0 and $T_{\text{eff}}$ = 200 K at $\sim$5 Gyr; a 10 $M_J$ planet will have a log g = 4.0 and $T_{\text{eff}}$ = 1800 K at $\sim$10 Myr. Radii range from 1.1 $R_J$ (200 K) to 1.2 $R_J$ (800 K) to 1.6 $R_J$ (1800 K). Free-floating planets have been discovered throughout this temperature range (e.g., Cushing et al. 2011; Faherty et al. 2016). The surface gravity has little effect on the strength of the signal for the small range of surface gravities for objects with $M < 13 M_J$, so we use a single representative surface gravity.

Briefly, we calculate temperature structures assuming radiative-convective equilibrium as described in McKay et al. (1989), Marley et al. (1996, 1999), Saumon & Marley (2008), and Morley et al. (2012, 2014). The opacity database for gases is described in Freedman et al. (2014). The abundances of molecular, atomic, and ionic species are calculated using a modified version of the NASA CEA Gibbs minimization code (McBride & Gordon 1992). We include
condensation of cloud species to remove materials from the gas phase, including water and HDO at cold temperatures. Descriptions of recent updates to opacities and chemical equilibrium are described in M. S. Marley et al. (2019, in preparation).

We calculate moderate-resolution spectra using these pressure−temperature and abundance profiles with the Morley et al. (2015) thermal emission code, which uses the open-source radiative transfer code disort (Stamnes et al. 1988), which calculates intensities and fluxes in multiple-scattering and emitting layered media using the discrete-ordinate method.

We include HDO and CH3D opacity when calculating moderate-resolution spectra. Cross sections are calculated using line lists from HITRAN 2012 for CH3D (Rothman et al. 2013) and ExoMol for HDO (Janca et al. 2003; Voronin et al. 2010) and are shown in Figure 2. Our canonical cases assume a protosolar D/H ratio of $2 \times 10^{-5}$, typical for formation conditions of stars in the Local Group; CH3D/CH4 is taken to be $4 \times D/H$ in all our simulations and HDO/H2O is $2 \times D/H$, the factors arising from the multiple H atoms in each methane and water molecule.

One of the strongest molecular features of CH3D is at $\sim 4.55 \mu m$. This wavelength region is a “window” in atmospheric opacity for cold brown dwarfs, since the important absorbers in the atmosphere—H2O, CH4, and NH3—have low opacity at these wavelengths. For a trace species like CH3D, a smaller amount of the species is necessary for it to be spectroscopically detectable at these window wavelengths because the path length through the atmosphere is longer. In contrast, HDO has features across the near- and mid-infrared (e.g., 3.7 $\mu m$), but these overlap with absorption features from the more abundant species.

4. Results

4.1. CH3D is More Observable than HDO

Examples of our model spectra are shown in Figure 3, for a model with $T_{\text{eff}} = 250$ K and surface gravity of 4.0, representing a $4–5 M_J$ object with an age of 2 Gyr. Here we show the regions with the strongest CH3D and HDO signals, respectively, for the temperature with the largest-amplitude HDO feature. We find that CH3D has a substantially stronger impact on the spectrum than HDO; this is true at all temperatures studied here.

To quantify the observability of CH3D and HDO, we simulate the G395H/F290LP grating/filter combination mode.
of James Webb Space Telescope (JWST)/NIRSpec (2.87–5.14 μm, R ~ 2700), using the JWST online exposure time calculator tool (Pontoppidan et al. 2016). We assume that each object is 10 pc away, to match the distances of known cold brown dwarfs (of the known Y dwarfs, 14 of those with measured distances are within 11 pc and 8 more are within 20 (Leggett et al. 2017)). We assume total observation times of 2.5 hr, including dither time. Dithering is necessary because above a signal-to-noise ratio (S/N) ~ 300, JWST is flat-field limited.10

While the 4.55 μm band of CH$_3$D is in one of the brightest wavelength regions for a cold brown dwarf, the 3.7 μm HDO band is within an absorption feature, so the brown dwarf is intrinsically fainter at those wavelengths. Spectra of cool brown dwarfs can therefore be measured at substantially higher S/N at 4.55 μm than 3.7 μm. Both the relative size of spectral features

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10 https://jwst-docs.stsci.edu/jwst-exposure-time-calculator-overview/jwst-etc-residual-flat-field-errors
and the underlying spectrum of the brown dwarf contribute to making CH₃D much easier to detect.

4.2. Minimum Resolving Power and Wavelength Ranges Needed

The molecular bands of CH₃D are relatively broad in wavelength (see Figure 2); however, to identify individual features within that broad band, a resolving power of ~1000 is required (see the bottom panel of Figure 3). The most useful wavelength range is from 4 to 5 μm; CH₃D also has a feature at 8.5 μm, but with a higher background and fainter source at longer wavelengths with JWST/MIRI, the 4–5 μm region is always favored.

4.3. Spectrum Signal-to-noise for D Detection

We calculate the signal to noise of the spectrum necessary to distinguish between a model with and without each deuterated species assuming a protosolar abundance (CH₃D/CH₄ = 4 × D/H = 8 × 10⁻⁵; HDO/H₂O = 2 × D/H = 4 × 10⁻⁶), using a chi-squared rejection test (Gregory 2005). We note that this is an imperfect method for claiming a “detection,” but remains an intuitive way for the reader to picture the relative ease of detection for different simulated spectra. We verify this approach against a full Bayesian retrieval in Section 4.6.

The S/N needed generally increases with increasing temperature. HDO always requires an S/N greater than 200 for a 10σ detection; CH₃D requires an S/N less than 200 for objects with temperatures ≤600 K. Water and HDO condensation at T_eff < 400 K decrease the strength of HDO absorption for the coldest models.

Figure 4 summarizes our results; in the top two panels, the shaded regions show the S/N achievable in 2.5 hr, and the symbols show the S/N required for a 10σ nominal detection of the deuterated species. We find that HDO is never detectable in our simulated observations in a 2.5 hr integration. CH₃D is detectable in objects between 200 and 800 K in <2.5 hr. The bottom panel shows the fraction of brown dwarfs expected to be less massive than the 13 M_J deuterium-burning limit based on a simulated population; cold brown dwarfs are likely to be low mass and present the best targets for deuterium searches.

4.4. Temperature Strongly Controls Presence of D Features

Figure 4 clearly shows that T_eff strongly affects the strength of both CH₃D and HDO features; low-temperature objects require lower-S/N spectra. This is due to an intrinsic property of molecular opacities: the peak-to-trough amplitude of molecular cross sections in the infrared is strongly correlated with temperature; this is shown for water vapor in Figure 2 (bottom panel). At 200 K, the water cross section between 2.5 and 4.5 μm varies between ~10⁻¹⁹ and 10⁻²⁷ cm²/molecule, while at 2000 K it varies between ~10⁻¹⁰ and 10⁻²² cm²/molecule. This striking difference—eight to two orders of magnitude difference between the absorption band and window—means that the window regions of cold objects probe relatively deeper layers. The larger column of material probed means that a feature from a trace species like CH₃D is more prominent in a colder object. This fact has been exploited for decades to detect trace species at ~5 μm in Jupiter, including CH₃D, PH₃, and GeH₄ (Bjoraker et al. 1986).

4.5. Effect of Enhanced Atmospheric Metallicity and D/H Ratio

The atmospheres of extrasolar Saturns and Neptunes may be significantly enhanced in metals. We simulate additional spectra with T_eff = 320 K, chosen to represent a young super-Neptune to Saturn-mass object (30–100 M_Earth) at 1–20 Myr. We aim to determine how the detectability of CH₃D scales with metal enhancement, using Jupiter-like (3 × solar), Saturn-like (10 × solar), and Neptune-like (100 × solar) metallicities and D/H ratios of 2 × 10⁻³ (protosolar) and 5 × 10⁻⁵ (Neptune-like). An example spectrum with high metallicity and enhanced D/H is shown in Figure 5.

The strength of the CH₃D feature scales with metallicity; increasing the metal enhancement by a factor of 10 decreases the signal to noise needed by a factor of ~3. Similarly, increasing the D/H ratio decreases the S/N needed. These results are summarized in the center panel of Figure 5.

The temperature evolution of Neptune- and Saturn-mass objects is shown in Figure 5, calculated using the
estimation tools to those presented in Line et al. (2015, 2017), but the model is upgraded to include PH₃ and CH₃D. We tailor the retrieval setup to match the atmospheric structure of a 300 K, log g = 5 (cgs), solar metallicity, cloud-free Y dwarf with D/H = 2 × 10⁻⁵. We freely fit the abundances of each species individually, pressure–temperature profile, surface gravity, temperature, and radius.

We find that we can constrain the ratio of CH₃D/CH₄ to (8.0 ± 0.2) × 10⁻⁵ with a 2.5 hr observation, assuming the same noise models as in Section 4.1, corresponding to a D/H ratio of (2.0 ± 0.05) × 10⁻⁵. These constraints are remarkable, but in these simulations the forward model is a perfect match to the data; hidden, unforeseen assumptions, or systematic errors will inhibit these constraints.

5. Discussion

5.1. Converting CH₃D/CH₄ to D/H

Above, we assumed CH₃D/CH₄ equals 4 × D/H (i.e., the molecules are in isotopic equilibrium). However, isotopic exchange depends on temperature. Deep, hotter layers are expected to be in isotopic balance, but colder upper layers probed by these measurements may not be. The actual CH₃D/CH₄ ratio is determined by a vertical mixing timescale and isotopic exchange timescale. At the top of the atmosphere, the relative abundance f of CH₃D/CH₄ compared to bulk D/H is 1.25 for Jupiter, 1.38 for Saturn, 1.68 for Uranus, and 1.61 for Neptune (Lecluse et al. 1996). The objects considered here are hotter than these planets, and would therefore be closer to isotopic balance (f = 1.0–1.25). Our approximation is conservative; if f is higher, the amount of CH₃D is larger and therefore easier to detect.

5.2. Clouds

Cloud opacity is not included in these calculations. Clouds typically mute features in thermal emission spectra, so if objects of interest are extensively cloudy, these species would be harder to observe. Brown dwarfs with T_eff > 1200 K have extensive refractory clouds (silicates/iron), while colder objects are relatively well matched by cloud-free models (e.g., Cushing et al. 2008) until water clouds form for objects less than 375 K (Morley et al. 2014). Using cold models with thick water ice clouds, we find that cloud-free simulations underestimate the S/N needed to detect CH₃D features by ~40%–50%.

5.3. Interior Physics, Masses, and Ages of the Coldest Brown Dwarfs

For objects with known masses, detecting deuterium could allow us to estimate their ages and test models of deuterium fusion as a function of mass. Our calculations demonstrate that deuterium is most observable in the coldest brown dwarfs, the Y dwarfs. The bottom panel of Figure 4 shows a simulation of the number of brown dwarfs at a given temperature, assuming that the initial mass function is a power law (index α = 1), and with a uniform age distribution between 0 and 10 Gyr (Saumon & Marley 2008). A 13 M_J object cools to 300 K in 10 Gyr, so for objects under ~300 K, all simulated objects have masses less than the deuterium-burning limit (M < 13M_J). For objects between 300 and 400 K, ~30%–68% have M < 13M_J; for hotter objects, the fraction of brown dwarfs with M < 13M_J

methodologies described in Lopez & Fortney (2014), assuming that Neptunes have high initial entropies (“hot start”) and cloud-free atmospheres. Young (10 Myr old) Saturn-mass objects are predicted to have temperatures around 400 K and cool to ~200 K within 100–300 Myr. Neptune-mass planets are colder, with temperatures around 250 K at 10 Myr. Planets in this mass range may be detectable with JWST (Beichman et al. 2010; Schlüter et al. 2016).

4.6. Retrieving D/H Ratios from JWST Spectra

Using the atmospheric retrieval tools recently applied to brown dwarfs (Line et al. 2015, 2017) we quantitatively determine the degree to which we can constrain the CH₃D/CH₄ ratio with NIRSpec on JWST assuming that our models perfectly represent real cold brown dwarfs. We use the identical forward model parameterization and Bayesian parameter
drops off to ∼1%–2% for $T_{\text{eff}} > 800$ K (Saumon et al. 1996; Spiegel et al. 2011).

Quantifying the presence of deuterium in a range of Y dwarf atmospheres tests the assumptions made in the simulation and thus the properties of field brown dwarfs. Recent work by Dupuy & Liu (2017) showed that nearby brown dwarfs with mass measurements have systematically younger ages (a median of 1.3 Gyr and an age interval of 0.4–4.2 Gyr for a sample of 10 systems) than the 0–10 Gyr range simulated here; thus, more of them are likely to be deuterium-rich. Sampling a range of 250–500 K objects would test this prediction and provide an independent way of measuring the age of local substellar objects.

5.4. Detecting Deuterium with High-dispersion Spectroscopy from Ground-based Telescopes

Mollière & Snellen (2019) recently showed that deuterium may be detectable for exoplanets from the ground using high-dispersion spectroscopy. They find that CH$_3$D may be detectable at 4.7 μm using current instruments for transiting planets below 700 K. Future ELT-class telescopes will allow detections for a wide range of planets. They also find that HDO is more challenging because methane shields HDO absorption. This technique will be complementary to the moderate-resolution spectroscopy with telescopes like JWST considered here.

5.5. Planet Formation and Envelope Accretion

In our own solar system, the two largest giant planets, Jupiter and Saturn, have D/H abundances consistent with the protosolar nebula, while the lower-mass Neptune and Uranus are enhanced by a factor of several due to accretion of ices during planet formation. Measuring deuterium enhancement or depletion in exoplanets allows us to test planet formation mechanisms in other systems. Multiplanet systems will be particularly valuable since the primordial D/H ratio varies within the galaxy.

JWST will be capable of detecting cool Jupiters and Neptunes around nearby M dwarfs (Beichman et al. 2010; Schlieder et al. 2016). Jupiter-mass exoplanets with ages of 100–300 Myr will have temperatures of 250–300 K (Fortney et al. 2008) and radii of 1.1–1.15 $R_{\text{J}}$, so if any such nearby planets are discovered with JWST, they will require comparable S/N spectra to the free-floating objects considered here to detect CH$_3$D.

Young objects (10 Myr) with masses twice that of Neptune are predicted to have temperatures around 200–225 K and radii around 6–9 $R_{\text{Earth}}$. If their atmospheres are enhanced in metals and in deuterium, CH$_3$D may be detectable in their spectra (see Section 4.5).

6. Conclusions

In this Letter, we have presented spectra of model brown dwarfs and free-floating planets including both HDO and CH$_3$D for objects from 200 to 1800 K. CH$_3$D requires a lower-S/N spectrum to detect than HDO at all temperatures. Colder objects have stronger spectral features due to the inherent properties of the cross sections of molecular species, which have larger differences in absorption between troughs and peaks at colder temperatures. For objects from 200 to 800 K, a protosolar D/H ratio of $2 \times 10^{-5}$ would be detectable in spectra with average S/N per spectral element between 20 and 100, readily achievable for these objects with 2.5 hr of integration time with JWST, assuming a typical distance of 10 pc. Colder objects will have stronger lines, but require more time to observe since they are fainter; warmer objects have weaker lines that are not readily observable with JWST.

The D/H ratio has been an important tracer of planet formation, gas accretion, and atmosphere evolution in the solar system since the 1970s when CH$_3$D was first detected in Jupiter. For brown dwarfs and free-floating planets in the near future, similar measurements will allow us to map their masses and ages and test models of their interior physics. For exoplanets from Neptune to Jupiter mass, D/H measurements will allow us to understand envelope accretion for planets outside the solar system. These measurements pave the way for future studies of terrestrial planets, for which D/H measurements trace the accretion of their atmospheres and their evolution over their lifetimes.

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References

Beer, R., Farmer, C. B., Norton, R. H., Martinchik, J. V., & Barnes, T. G. 1972, Sci, 175, 1360
Beichman, C. A., Krist, J., Trauger, J. T., et al. 2010, PASP, 122, 162
Bjoraker, G. L., Larson, H. P., & Kunde, V. G. 1986, Icar, 66, 579
Chamberlain, J. W., & Hunten, D. M. 1987, Theory of Planetary Atmospheres. An Introduction to Their Physics and Chemistry (Orlando, FL: Academic Press Inc.), 368
Charbonneau, D., Brown, T. M., Noyes, R. W., & Gilliland, R. L. 2002, ApJ, 568, 377
Cleeves, I. L., Bergin, E. A., Alexander, C. M. O., et al. 2014, Sci, 345, 1590
Courtin, R., Gautier, D., Marten, A., Bezard, B., & Hanel, R. 1984, ApJ, 287, 899
Cushing, M. C., Kirkpatrick, J. D., Gelino, C. R., et al. 2011, ApJ, 743, 50
Cushing, M. C., Marley, M. S., Saumon, D., et al. 2008, ApJ, 678, 1372
de Bergh, C., Lutz, B. L., Owen, T., Braault, J., & Chauville, J. 1986, ApJ, 311, 501
de Bergh, C., Lutz, B. L., Owen, T., & Maillard, J.-P. 1990, ApJ, 355, 661
Donahue, T. M., & Pollack, J. B. 1983, in Venus, ed. D. M. Hunten et al. (Tucson, AZ: Univ. Arizona Press), 1003
Drake, M. J. 2005, M&PS, 40, 519
Drake, M. J., & Righter, K. 2002, Nat, 416, 39
Dupuy, T. J., & Liu, M. C. 2017, ApJS, 231, 15
Espinoza, N., Fortney, J. J., Miguel, Y., Thorgren, D., & Murray-Clay, R. 2017, ApJL, 838, L9
Faherty, J. K., Riedel, A. R., Cruz, K. L., et al. 2016, ApJS, 225, 10
Feuchtinger, H., Lellouch, E., Bézard, B., et al. 1999, A&A, 341, L17
