SIMULTANEOUS DETECTION OF WATER, METHANE, AND CARBON MONOXIDE IN THE ATMOSPHERE OF EXOPLANET HR 8799 b

TRAVIS S. BARMAN1, QUINN M. KONOPACKY2,3, BRUCE MACINTOSH4,5, AND CHRISTIAN MAROIS6
1 Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721 USA; barman@lpl.arizona.edu
2 Center for Astrophysical and Space Science, University of California San Diego, La Jolla, CA, 92033, USA
3 Dunlap Institute for Astronomy and Astrophysics University of Toronto, Toronto, Ontario, M5S 3H4, Canada
4 Kavli Institute for Particle Astrophysics and Cosmology, Stanford University, Stanford, CA 94305 USA
5 Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, USA
6 NRC Herzberg Astronomy and Astrophysics, 5071 West Saanich Rd, Victoria, BC V9E 2E7, Canada

ABSTRACT

Absorption lines from water, methane, and carbon monoxide are detected in the atmosphere of exoplanet HR 8799 b. A medium-resolution spectrum presented here shows well-resolved and easily identified spectral features from all three molecules across the K band. The majority of the lines are produced by CO and H2O, but several lines clearly belong to CH4. Comparisons between these data and atmosphere models covering a range of temperatures and gravities yield log mole fractions of H2O between −3.09 and −3.91, CO between −3.30 and −3.72, and CH4 between −5.06 and −5.85. More precise mole fractions are obtained for each temperature and gravity studied. A reanalysis of H-band data, previously obtained at a similar spectral resolution, results in a nearly identical water abundance as determined from the K-band spectrum. The methane abundance is shown to be sensitive to vertical mixing and indicates an eddy diffusion coefficient in the range of 10^6–10^8 cm^2 s^−1, comparable to mixing in the deep troposphere of Jupiter. The model comparisons also indicate a carbon-to-oxygen ratio (C/O) between ~0.58 and 0.7, encompassing previous estimates for a second planet in the same system, HR 8799 c. Super-stellar C/O could indicate planet formation by core-accretion; however, the range of possible C/O for these planets (and the star) is currently too large to comment strongly on planet formation. More precise values of the bulk properties (e.g., effective temperature and surface gravity) are needed for improved abundance estimates.

Key words: brown dwarfs – planetary systems – stars: atmospheres – stars: low-mass

1. INTRODUCTION

The HR 8799 planetary system remains unique as the only system to have multiple, directly imaged, planets (Marois et al. 2008, 2010). Four planets orbiting HR 8799 have been monitored regularly since their discovery, providing the astrometric data needed to estimate their orbital properties and masses. The current astrometric data indicate that all four planets are less than 13 M_Jup (Fabrycky & Murray-Clay 2010; Marois et al. 2010; Currie et al. 2011; Pueyo et al. 2014).

The planets are frequently observed for the purposes of characterizing their atmospheric properties and, in particular, their chemical compositions. The two outer most planets, b and c, have the most comprehensive wavelength coverage including near-infrared (near-IR) spectroscopy at low, R ~50–100 (Bowler et al. 2010; Barman et al. 2011a; Oppenheimer et al. 2013) and medium, R ~4000 (Konopacky et al. 2013) resolutions. The Gemini Planet Imager (GPI) has measured low-resolution spectra of planets c and d (Macintosh et al. 2014; Ingraham et al. 2014). Spectroscopy of multiple planets orbiting HR 8799 allows direct comparisons of atmospheric compositions for a coeval set of planets formed from the same protoplanetary disk. The only other planetary system for which such a comparison is currently feasible is our own Solar System.

The giant planets in our Solar System were likely born with bulk compositions determined by their initial location in the planetary disk and the specific solid-to-gas (M_sol/M_gas) accretion history they experienced. As these initially hot planets cooled with time, their atmospheres experienced various levels of vertical mixing and condensation. The atmospheric composition may have been further altered by continued accretion of solid bodies or mixing with a deep metal-rich core. Consequently, the present-day mole fractions for important trace molecules (H2O, CH4, CO2, CO, NH3, and N2) of giant planets in our Solar System are the result of numerous chemical and physical processes. Inferring elemental abundances from molecular abundances requires a clear understanding of the atmospheric chemical and dynamical history. Even for Jupiter and Saturn, only upper limits on carbon-to-oxygen ratio (C/O) have been measured, a poignant reminder of how challenging such measurements can be (Wong et al. 2004; Visscher & Fegley 2005). Despite this complex connection between present-day composition and the composition at birth, it remains plausible that the present-day molecular abundances hold clues pertaining to the formation history of our giant planets. By observing young giant planets, like those orbiting HR 8799, the effect of billions of years of atmospheric evolution that blurs the connection between atmospheric properties and the formation process is avoided.

Presented below are new observations of HR 8799 b that provide comparable wavelength coverage, spectral resolution and signal-to-noise ratio (S/N) as similar observations of HR 8799 c that revealed individual resolved water and carbon monoxide absorption features (Konopacky et al. 2013, hereafter K13). For HR 8799 b, the mole fractions of these two molecules as well as methane are determined using well-resolved spectral features. From these mole fractions, the coefficient of eddy diffusion (K_D) and C/O are estimated.
2. OBSERVATIONS AND SPECTRUM EXTRACTION

HR 8799 b was observed in 2013 on July 25, 26, and 27 (UT) with the OSIRIS instrument (Larkin et al. 2006) in the K band using an identical instrument configuration as in previous work by this group (Barman et al. 2011a, hereafter B11) resulting in 5.2 hr of on-target integration time under good observing conditions. The data were calibrated and rectified to produce three-dimensional basic calibrated data cubes (Krabbe et al. 2004). The data were initially binned to $R \sim 100$ and speckles were suppressed following B11. As in B11, at low-$R$, the spectrum S/N is limited by residual correlated speckle noise. Despite the increase in signal from combining the same spectrum $S/N$ is limited by residual correlated speckle noise. The $K$-band spectrum was absolute flux calibrated using the $K_s$ magnitude ($M_K = 14.15 \pm 0.1$) reported in B11.

At the full resolution and sampling provided by OSIRIS, errors in flux are correlated across several wavelength channels and may alter the relative depth of narrow absorption features. Subtracting the continuum, modeled as a smoothed version of the observed spectrum, removes many residual speckle artifacts that vary smoothly with wavelength (K13). Inevitably, however, speckle artifacts that depend more strongly on wavelength (e.g., produced by optics near the focal plane) likely remain even in a continuum-subtracted spectrum. Despite potential lingering artifacts, this strategy worked well in K13 and is adopted here using the ensemble of data from 2009 through 2013, median-combined into a single spectrum. Given the wide angular separation of HR 8799 b, residual speckle artifacts should be less severe than they were for HR 8799 c. The rms uncertainties in the continuum-subtracted spectrum closely match the photon-noise limit. The low-$R$ spectra from various observing runs show no significant differences across this four year time frame and intrinsic variability would likely occur over timescales of days rather than years and impact broader wavelength ranges than the spectral lines of interest.

3. MODEL SPECTRA

For this study, the grid of exoplanet atmosphere models described in B11 was updated to include the methane linelist from Yurchenko & Tennyson (2014) supplemented with optical opacities from Karkoschka & Tomasko (2010). The former update added approximately 10 billion transitions to the overall molecular opacities and improves the accuracy of line strengths at high temperatures—across the $K$-band alone there are roughly a billion transitions. The methane abundance is low in non-equilibrium chemistry models appropriate for HR 8799 b (B11) and, consequently, there were only minor changes to the model atmosphere structures after this opacity update. Nevertheless, the ExoMol methane list is currently the most accurate and complete list available and the observations analyzed here have a resolution where accurate line data are important when studying atmospheric abundances.

The opacity of solid and liquid particles suspended in the atmosphere (clouds) is included using the parameterized intermediate cloud model described in B11. Briefly, the lower boundary of the clouds is determined by chemical equilibrium while the upper boundary is described by an exponential decay that begins at a specified pressure. This outer pressure is a free parameter that establishes the cloud thickness, allowing for a range of models with cloud opacity between the high (DUSTY) and cloud-free (COND) cases often used to bracket the importance of clouds (Allard et al. 2001). The particle size distribution is log-normal with a mean size set to 5 $\mu m$. Cloud thickness plays an important role in determining the overall spectral shape and is included as a free parameter in the model fits discussed below (following B11).

Synthetic spectra were calculated with a wavelength sampling of 0.05 $\AA$ from 1.4 to 2.5 $\mu m$. Each of these synthetic spectra was convolved with a Gaussian kernel with FWHM matching the OSIRIS spectral resolution before interpolating onto the observed wavelength grid. These medium-resolution spectra were continuum-subtracted following the steps in K13.

4. RESULTS

4.1. HR 8799 b Versus c

Figure 1 compares the $R \sim 4000$ spectrum of HR 8799 b to that of HR 8799 c. Both exoplanet spectra contain a similar set of absorption features, with most of the similarities at wavelengths of prominent H$_2$O absorption; however, most lines are deeper in the spectrum of b. The CO (2,0) band-head at $\sim 2.3 \mu m$ is detected now with medium spectral resolution but only marginally present at low-$R$ (B11). This band-head appears slightly deeper and has a shallower slope in the spectrum of b than c, the result of stronger water absorption and additional CH$_4$ lines for HR 8799 b in this wavelength range. Three regions of CH$_4$ absorption are visually identifiable between 2.15 and 2.4 $\mu m$ (lower panel of Figure 1). The strongest methane lines are seen around 2.32 and 2.37 $\mu m$. None of these features are present in the spectrum of c, consistent with the methane non-detection reported by K13. A few additional CH$_4$ lines are marginally identified around 2.25 $\mu m$, however, many of the weaker CH$_4$ lines overlap with those of H$_2$O and CO, making visual identification difficult.
4.2. Cross-correlation

As an additional confirmation that spectral features from all three molecules are present in the OSIRIS spectrum of HR 8799 b, a cross-correlation analysis was used following K13. In this case, a new CH₄ template was calculated using roughly a billion of the strongest transitions across the K band (Yurchenko & Tennyson 2014). Water and CO templates were calculated using lists from Barber et al. (2006) and Goorvitch (1994). Figure 2 compares the cross-correlation functions (CCFs) for each template. Peaks in the CCFs are found for all three molecules at identical velocities, centered on zero km s⁻¹. As was the case for HR 8799 c, a peak with maximum near 1 is found for H₂O, indicating that this molecule contributes most of the spectral lines. CO also shows the characteristic ringing pattern, produced by near-repeating patterns of CO lines, many separated by roughly 200 km s⁻¹ in velocity. This same CCF pattern was found for CO in HR 8799 c by K13, with peak of 0.6 compared to 0.4 here. A peak in the CCF for CH₄ is present, but not as prominent as found for H₂O, mainly because much of the weak-line information is blended with other stronger lines at this resolution.

H-band observations were previously obtained using the same telescope and instrument combination as used for K-band and were originally analyzed at low resolution in B11. These data have been reanalyzed and continuum-filtered at full resolution (also R ~ 4000) following the same steps as K-band. The average S/N of these data is about 3 times lower than the K-band data and show a pattern of lines that are visually difficult to identify. B11 concluded that water is the dominant molecular opacity source in this wavelength range and this is confirmed here by a cross-correlation analysis. The CCFs for H₂O and CH₄ templates across the H band are plotted in Figure 3. Correlating the data with an H-band H₂O template yields a strong peak in the CCF (Figure 3). No peak was detected for an H-band CH₄ template (using the ExoMol list).

The HR 8799 b K-band spectrum also correlates well with the HR 8799 c spectrum, another indication that both planet spectra share similar spectral patterns of H₂O and CO lines. The CCF was also recalculated for HR 8799 c using the new CH₄ template and no peak was found, confirming the non-detection of CH₄ reported by K13.

4.3. Model Comparisons

For the atmospheric abundance study presented below, it is important that the underlying thermal structure of the models, especially across most of the photosphere, is reasonably correct. Atmospheres of giant planets are generally close to local thermodynamic equilibrium and, thus, a model matching the planet’s spectral energy distribution over a wide wavelength range should have a thermal profile that reasonably approximates the planet’s average thermal structure. A similar model comparison as performed by B11 was repeated, but comparing updated models with the new CH₄ list to the new medium-resolution unfiltered spectrum discussed above and additional flux calibrated data spanning 1–5 μm. For wavelengths less than 1.8 μm the z/Y-band flux of Currie et al. (2011), the low-R P1640 J-band spectrum (Oppenheimer et al. 2013) and the H-band spectrum from B11 were used. Photometric data was used at wavelengths longer than 3 μm (Galicher et al. 2011; Skemer et al. 2012; Currie et al. 2014). The data used for the model fits are plotted in Figure 4.

The relative flux calibration of the near-IR spectra from OSIRIS and P1640 could impact the model comparisons, as these spectra are calibrated using H and Ks photometry that have a range of reported values and uncertainties (Marois et al. 2008; Metchev et al. 2009; Esposito et al. 2013). It is also possible that HR 8799 b is variable as indicated by studies of brown dwarfs (Metchev et al. 2015). Such potential issues are not accounted for here and the H and K flux calibration described in B11 is used. A small scaling was applied so that the H-band portion of the P1640 spectrum matches the H-band OSIRIS spectrum, resulting in a slight change in the absolute fluxes of the P1640 J-band spectrum plotted in Figure 4.
Example spectra of the best matching solar abundance models are plotted in Figure 4, for a range of $T_{\text{eff}}$ between 900 and 1100 K and $\log(g)$ between 3.0 and 4.0. The best matching model has the same gravity as found previously by B11 ($\log(g) = 3.5$) but cooler ($T_{\text{eff}} = 1000$ K). Across the near-IR, the model spectra do a reasonable job of reproducing the observations. When fitting the observations (photometric and spectroscopic), all data are weighted equally. Between 3 and 5 μm, however, the model comparisons to available photometric data (from a variety of telescopes, epochs, and image processing methods) show disagreements at $L'$ and $\sim 4$ μm. Similar levels of disagreement at this wavelength are seen in other model comparisons (Marley et al. 2012; Skemer et al. 2012; Currie et al. 2014). These photometric observations probe similar atmospheric depths and, therefore, pull model fits in opposite directions in both $T_{\text{eff}}$ and $\log(g)$. Further observations across this spectral region are probably warranted. Previous studies of HR 8799 b result in a range of $T_{\text{eff}}$ between 750 and 1200 K and $\log(g)$ between 3 and 4.5 (see Marley et al. 2012, their Table 1), encompassing the range explored here.

Model atmosphere parameters are sometimes intentionally biased to match predictions of cooling tracks, providing guaranteed consistency between $T_{\text{eff}}$, $\log(g)$, and $L_{\text{bol}}$ and mass/radius expectations. Such forced agreement can be useful, but is not done here. More important is finding a range of atmospheric temperature–pressure (T–P) profiles that yield pseudo-continua that are as consistent as possible with the observed spectral energy distribution. Good agreement between bulk parameters found by atmosphere-only fitting and those inferred from cooling tracks, age, and luminosity can be challenging for low-temperature planet-mass objects, likely a result of the complexity of their atmospheres which are not reproducible by time-independent one-dimensional models with simplistic cloud prescriptions. Consequently, conservative ranges of $\log(g)$ ($\pm 0.5$) and $T_{\text{eff}}$ ($\pm 100$ K) around the best matching values are used for the abundance analysis discussed below, despite potential inconsistencies with cooling track predictions at the high and low ends of these ranges.

### 4.4. Mole Fractions of CO, CH$_4$, and H$_2$O

At low spectral resolution, the slopes on either side of the $K$-band peak are very similar to those seen in substellar atmospheres where water is the dominant opacity source. B11 showed (their Figure 14) that CO and CH$_4$ likely contribute to the $K$-band opacity but, at low resolution, the CO band head was not confidently detected nor any significant hints of CH$_4$, making it difficult to assess their relative importance. Bowler et al. (2010) also found no evidence of methane absorption in their narrow-band spectrum covering $\sim 2.1$–$2.2 \mu$m. With resolved absorption features from all three molecules identified, their individual abundances can now be determined.

Evidence for quenching of CO and CH$_4$ in the atmospheres of the HR 8799 planets has been established elsewhere (Hinz et al. 2010; Barman et al. 2011a; Marley et al. 2012; Skemer et al. 2012). An important consequence of this mixing-induced non-equilibrium chemistry is that the mole fractions should be nearly independent of height across the photosphere. The absence of height-dependence greatly simplifies the parameterization of the mole fractions, allowing straightforward model fitting using standard $\chi^2$ minimization.

The mole fractions are determined sequentially by computing grids of synthetic spectra (continuum filtered) with scaled molecular abundances for nine different T–P profiles corresponding to $T_{\text{eff}} = 900$, 1000, and 1100 K and $\log(g) = 3.0$, 3.5, and 4.0. These temperatures and gravities bracket those found when comparing models to the broad wavelength data shown in Figure 4. A spectrum is calculated for each mole fraction value and model T–P profile. The mole fractions of CO, CH$_4$, and H$_2$O are each scaled from 0 to 1000 relative to their non-equilibrium solar abundance values using a uniform logarithmic sampling (resulting in 100 synthetic spectra per T–P profile).

The mole fraction of H$_2$O was determined first, keeping CO and CH$_4$ at their solar values. To avoid biasing in the H$_2$O mole fractions caused by overlapping CO or CH$_4$ lines, the fit was restricted to wavelengths less than the CO band head, while masking the strongest CH$_4$ line region (near $2.2 \mu$m). Following this step, a second grid of synthetic spectra was calculated with the H$_2$O mole fraction equal to the best-fit value from the previous step, CH$_4$ at its solar value, and now mole fractions of CO scaled as previously done for H$_2$O. In this case, only wavelengths greater than (and including) the CO band head were fit, while masking the strong CH$_4$ line near 2.32 and 2.37 μm. In the final step, using the best-fitting H$_2$O and CO mole fractions, a third grid of synthetic spectra was made with scaled CH$_4$ mole fractions. Only the strongest CH$_4$ lines from 2.2 to 2.37 μm were included in this fit.

The model with the overall lowest $\chi^2$ from this three-step fitting process has a slightly lower gravity ($\log(g) = 3.0$) than the best matching solar abundance model compared to the full spectral energy distribution (SED). The $\chi^2$ distributions for the mole fractions in this model are plotted in Figure 5, with log mole fractions of H$_2$O, CO, and CH$_4$ that are $-3.85 \pm 0.01$, $-3.67 \pm 0.02$, and $-5.85 \pm 0.04$, respectively, with the model spectrum compared to the $K$-band observations in Figure 6.
Both H$_2$O and CO are about half the non-equilibrium solar value, while CH$_4$ is about 15 times lower than the non-equilibrium solar value (see vertical dashed lines in Figure 5). The best matching mole fractions for each $T_{\text{eff}}$ and $\log(g)$ are listed in Table 1, with formal 1σ errors determined from the $\chi^2$ distributions. These values can be compared to the range of solar (non-equilibrium) mole fractions by using Figure 12 (see vertical dashed line), discussed below.

The filtered $K$-band spectrum is used to determine the molecular abundances primarily because it is a single data set from a single instrument with uniformly characterized uncertainties. It is important, however, to verify that the resulting mole fractions still yield spectra that are in reasonable agreement with the full SED. Figure 7 compares model spectra to the full SED for three different $T_{\text{eff}}$ and $\log(g)$ values and corresponding mole fractions listed in Table 1, and the comparisons remain good across the near-IR. The thermal IR includes absorption bands from CH$_4$, CO, and CO$_2$, providing a potential secondary test of the abundances. In all cases, the model flux at 3.3 µm, which probes a methane fundamental absorption band, is close to the observed value. The fluxes across the CO and CO$_2$ absorption bands between 4 and 5 µm changes considerably for the range of values found here; however, the observed ground-based photometry, with measurements on either side of the absorption bands, do not probe CO or CO$_2$ absorption well.

### Table 1

| Molecule | $T_{\text{eff}}$ | 3.0 | 3.5 | 4.0 |
|----------|-----------------|-----|-----|-----|
| H$_2$O   | 900             | $-3.82 \pm 0.01$ | $-3.39 \pm 0.01$ | $-3.09 \pm 0.01$ |
|          | 1000            | $-3.85 \pm 0.01$ | $-3.55 \pm 0.01$ | $-3.12 \pm 0.01$ |
|          | 1100            | $-3.91 \pm 0.01$ | $-3.58 \pm 0.01$ | $-3.24 \pm 0.01$ |
|          | 900             | $-3.61 \pm 0.02$ | $-3.48 \pm 0.02$ | $-3.30 \pm 0.02$ |
| CO       | 1000            | $-3.67 \pm 0.02$ | $-3.61 \pm 0.02$ | $-3.33 \pm 0.02$ |
|          | 1100            | $-3.72 \pm 0.02$ | $-3.61 \pm 0.02$ | $-3.30 \pm 0.02$ |
|          | 900             | $-5.85 \pm 0.04$ | $-5.55 \pm 0.04$ | $-5.18 \pm 0.04$ |
| CH$_4$   | 1000            | $-5.85 \pm 0.04$ | $-5.48 \pm 0.04$ | $-5.12 \pm 0.04$ |
|          | 1100            | $-5.79 \pm 0.04$ | $-5.42 \pm 0.04$ | $-5.06 \pm 0.04$ |

Figure 5. $\chi^2$ distributions for H$_2$O, CO, and CH$_4$ mole fractions when fitting model spectra with $T_{\text{eff}} = 1000$ K and gravity of $10^3$ cm s$^{-2}$ to the $K$ (solid) and $H$ (dashed) bands. Vertical dotted lines indicate the best-fit mole fractions and vertical dashed lines indicate solar (non-equilibrium) mole fractions. CH$_4$ was not detected in the $H$-band data, with a 3−σ upper limit of $10^{-5.6}$.

Figure 6. Top: continuum-subtracted spectrum for HR 8799 b (black) compared to the $T_{\text{eff}} = 1000$ K and $\log(g) = 3.0$ model with abundances equal to those found in Figure 5. Bottom: spectrum of HR 8799 b (black) compared to the same model plotted above, but with continuum intact.

Figure 7. Same observations as plotted in Figure 4, but compared to model spectra with non-solar H$_2$O, CO, and CH$_4$ mole fractions (see Table 1).
As discussed above, H$_2$O is detected in the med-resolution H-band spectrum by cross-correlation (Figure 3). Mole fractions for H$_2$O were obtained by fitting the H-band data in a similar manner as for the K band, using synthetic spectra with scaled H$_2$O and CH$_4$ mole fractions. A clear $\chi^2$-minimum was found for water for the same mole fraction as found by fitting the K-band spectrum, but with much larger uncertainties. CH$_4$ was not detected (consistent with the cross-correlation test) and only an upper limit was found (see the dashed lines in Figure 5).

The mole fractions determined above are sensitive to the thermal profile, surface gravity, individual line broadening parameters, and potential residual artifacts in the data. Uncertainties associated with these properties are difficult to quantify without a more complex statistical analysis of the model comparisons and is beyond the intended scope of this paper. For example, the mole fractions depend on the model atmosphere surface gravity, but it is unlikely that the planet’s gravity falls outside the range explored here, given the limits placed on gravity by other data. The details of the cloud properties (coverage and thickness) are partially mitigated by the continuum subtraction process but may still impact the inferred mole fractions indirectly through degeneracies in the surface gravity and effective temperature estimation. Uncertainties in $T_{\text{eff}}$ translate into small (∼0.1 dec) changes in the mole fractions. Future refinement of the mole fractions will benefit most by improved determinations of log g. Surface gravity broadens spectral lines and, in principle, the width of auto-correlation functions for models of various surface gravities could be used to determine gravity’s contribution to the total line broadening. Unfortunately, even a resolution of 4000 (∼75 km s$^{-1}$) is too low for such an exercise to yield better gravity estimates than those based on model fits to lower resolution data (e.g., fitting shapes of H and K band spectra).

4.5. Estimating $K_{zz}$

Vertical mixing is often characterized by the coefficient for eddy diffusion ($K_{zz}$) where the vertical mixing timescale above the convection zone is $L_{\text{eff}}/K_{zz}$ and $L_{\text{eff}}$ is an effective length scale usually a few tenths the pressure scale height (Smith 1998). Below the point in the atmosphere where the mixing timescales are shorter than chemical reaction timescales, the atmosphere will be in chemical equilibrium. Most chemical reactions are fast; however, the reactions governing CO and CH$_4$ have one or more rate-limiting steps that result in long chemical timescales (Visscher et al. 2010; Zahnle & Marley 2014) that rapidly increase with decreasing density, quickly exceeding the age of the planet by many orders of magnitude. The ultimate consequence is that, for plausible values of $K_{zz}$, the photospheric mole fractions of CO and CH$_4$ (as well as others, e.g., N$_2$, NH$_3$, and CO$_2$) may no longer depend on the photosphere conditions but instead on the conditions deeper in the atmosphere where the chemical and mixing timescales become comparable.

The detection of CO in Jupiter’s atmosphere is an excellent example of vertical mixing in action. For the very low temperatures in Jupiter’s atmosphere (∼100 K), the majority of carbon is in CH$_4$ at an abundance that is essentially constant with height. Therefore, if quenching occurs in the atmosphere, the photospheric CH$_4$ will be unchanged. The equilibrium photospheric mole fractions of CO, on the other hand, are small and rapidly decreasing with height. If pure chemical equilibrium persisted throughout, CO would be nearly impossible to observe. However, photospheric CO absorption has been measured, which revealed evidence that non-equilibrium chemistry is at work, and the CO abundance has been used to estimate the value of $K_{zz}$ (Fegley & Lodders 1994).

In the atmospheres of young giant exoplanets as hot as HR 8799 b (∼1000 K) the situations for CO and CH$_4$ are reversed (Barman et al. 2011b; Zahnle & Marley 2014). At pressures between 1 and 10 bar, the temperatures are hot enough for CO to be thermochemically favored over CH$_4$. Also, the quenching can occur at or near depths where equilibrium mole fractions are height-dependent for CH$_4$ and nearly height-independent for CO. An important outcome is that, much like CO in Jupiter, measurements of CH$_4$ can be used to estimate $K_{zz}$ in the atmospheres of planets like HR 8799 b.

The photospheric CH$_4$ mole fractions versus $K_{zz}$ are plotted in Figure 8 for solar composition and a range of $T_{\text{eff}}$ appropriate for HR 8799 b. Only for log$(K_{zz}) > 10$ does $K_{zz}$ become independent of CH$_4$. The range of inferred mole fractions for methane (horizontal shaded region in Figure 8) indicate log$(K_{zz})$ around 7 for $T_{\text{eff}} = 1000$ K; however, the mole fractions at the quenching depth are temperature and gravity dependent leading to an uncertainty in $K_{zz}$ of about 100 cm$^2$ s$^{-1}$. Large departures from solar C and O abundances could change the inferred $K_{zz}$; however, as argued below, it is unlikely that C/O is very far from solar.

4.6. C/O Ratio

The C/O ratio for HR 8799 c was found to be slightly above that of the host star, tentatively favoring the core-accretion (CA) formation scenario over gravitational instability (K13). Determining the C/O for HR 8799 b is an important next step in understanding the formation history of this planetary system.

The photosphere of HR 8799 b is not in chemical equilibrium, as discussed above, with both CO and H$_2$O quenched deep in the atmospheres. Deep quenching of carbon and oxygen-bearing molecules has important implications for inferring the relative C and O element abundances from the molecular mole fractions. Even young giant planets, still hot
from recent formation, have atmospheres cool enough to allow solids and liquids to form, including silicate grains (e.g., MgSiO$_3$, Mg$_2$SiO$_4$). The abundance of these grains is limited by the overall abundance of Si, and will sequester a non-negligible fraction of the oxygen atoms. The photosphere of HR 8799 b is well below the temperatures needed for condensation to occur and, as a result, the inventory of oxygen should account for both the mole fractions of silicate grains and oxygen-bearing molecules. However, for the atmosphere of HR 8799 b, models indicate that the temperature at the quenching depths is above 2000 K and, thus, above the condensation temperature for major oxygen-depleting grains. In the case of the HR 8799 planets, non-equilibrium chemistry simplifies the C/O ratio dependence on atmospheric mole fractions ($N$) to
\[
\frac{C}{O} = \frac{N(\text{CH}_4) + N(\text{CO})}{N(\text{H}_2\text{O}) + N(\text{CO}_2)},
\]
and for small amounts of CH$_4$, the C/O ratio is determined by H$_2$O and CO alone.

Equation (1) and the mole fractions determined above (Table 1) for each model atmosphere $T_{\text{eff}}$ and $\log(g)$, results in C/O values between 0.4 and 0.7. This large range in C/O is mostly driven by the comparably large range of acceptable values for $\log(g)$, with C/O decreasing as $\log(g)$ increases. The mole fractions for the best matching model yield C/O = 0.61 ± 0.05 (with 1σ error determined from the formal errors in Table 1). Figure 9 compares the continuum-filtered observations to the best overall model from Section 4.6 (C/O = 0.61) and models with high and low C/O, to illustrate the changes in the spectrum as the relative molecular abundances change.

5. ATMOSPHERIC COMPOSITION AND FORMATION

If giant planets form primarily by a quick one-step process via gravitational instabilities, their atmospheres should have element abundances equal to the host star (Helled & Schubert 2009). On the other hand, if giant planets form primarily by the multi-step CA process, a range of element abundances are possible (Öberg et al. 2011). The abundances of a gas giant’s atmosphere formed via CA primarily depend on the location of formation relative to the frost lines for major carbon and oxygen bearing molecules in the disk (namely H$_2$O, CO$_2$, and CO) and the amount of solids acquired by the planet during the runaway accretion phase. The four planets orbiting HR 8799 offer an excellent opportunity to test this idea. Each planet currently orbits between the H$_2$O and CO$_2$ frost lines and potentially built up atmospheres from gas with similar amounts of solids.

In K13, the observed continuum-filtered spectrum of HR 8799 c was compared to atmosphere models restricted to a sequence of C and O element abundances derived from the Öberg et al. (2011) chemical model. The Öberg et al. model provides values for the C and O abundances, relative to the stellar values, for different amounts of solid accretion during the buildup of the planetary envelope. These abundances are plotted in Figure 10 for planets forming between the H$_2$O and CO$_2$ frost lines. In this model, both C and O abundances are linear functions of solid accretion, $M_{\text{solid}}/M_{\text{gas}}$, with slope and intercept set by the fraction of C (or O) sequestered by condensate formation and the overall grain/gas fraction in the disk. These assumptions are based on observations of protoplanetary disks and the interstellar medium (see Table 1 of Öberg et al. 2011). Solar C and O abundances have been suggested for HR 8799 (Sadakane 2006) and are adopted as the baseline here (Asplund et al. 2009). It should be noted, however, that this star is a λ-boo type star with solar C, N, and O abundances but sub-solar Fe-peak elements.

A high level of solid accretion during planet formation raises both C and O abundances, with O abundances increasing more rapidly than C for the simple reason that H$_2$O-ice is the most abundant solid between the H$_2$O and CO$_2$ frost lines. The combined effect is C/O decreasing as $M_{\text{solid}}/M_{\text{gas}}$ increases. The model proposed by Öberg et al. is a simple prescription for a complex process and, consequently, deviations from this model are to be expected. Despite its simplicity, the predicted C and O
abundances provide an ideal baseline for testing potential outcomes of CA formation specific to the HR 8799 system.

In order to make a direct comparison to the K13 results, the observed spectrum of HR 8799 b was analyzed in a similar manner as HR 8799 c. Given the CH4 update made to the model atmospheres, the fit was repeated for HR 8799 c. Only the C/O values for atmosphere accretion occurring between the H2O and CO2 frost lines (the current locations of all four HR 8799 planets) were used (see Figure 10). A χ2 was calculated for each continuum-subtracted synthetic spectrum in the T eff and log(g) range described above. The resulting χ2 distributions are plotted in Figure 11. The best-matching C/O for HR 8799 b is 0.66±0.04 and the revised best-matching C/O for HR 8799 c is 0.64±0.14, closely matching K13, but with a broader χ2 distribution. The new ExoMol methane absorption strengths across the K-band are lower than those from the Warmbier et al. (2009) linelist used in the K13 analysis resulting in smaller χ2 values for larger C/O and, hence, a broader distribution of χ2.

The K-band continuum shape can also be used to estimate the relative abundance of H2O and CO. Given the wider angular separation of b than c (1.7 versus 1″) from the star, the continuum of b is less affected by residual speckles. The observed spectrum, with continuum intact, was compared to the same set of atmosphere models and C and O abundances. The χ2 distribution from this comparison is plotted in the top panel of Figure 11 and shows both planets having C/O between ∼0.55 and 0.7, for similar Δχ2 as in the continuum filtered comparison.

The mole fractions of H2O, CO, and CH4 in the photosphere of the best-matching CA-specific atmosphere model can be compared to those found in Section 4.4, where the molecular abundances were determined to be independent of any formation model. The mole fractions for the CA-specific atmosphere models are plotted in Figure 12 as functions of C/O, for the range of T eff and log(g) explored here. Solar (non-equilibrium) mole fractions and solar C/O are indicated in this figure by the vertical dashed line. The CA-specific atmosphere model with C/O ∼ 0.66 has H2O and CH4 mole fractions that closely match those found in Section 4.4. These values are plotted as red symbols with horizontal and vertical error-bars. The different model fitting procedures result in consistent mole fractions for H2O and CH4, while the scaling procedure results in CO lower than in all of the model atmospheres with Öberg et al. based C and O abundances.
that the CO line broadening in the atmosphere models is under (or over) estimated, resulting in systematic errors in the inferred abundances (this will be investigated in a future paper).

Compared to H$_2$O and CH$_4$, CO has the weakest dependence on C/O, CH$_4$ and H$_2$O, however, are fairly sensitive to C/O, but their mole fractions can be small (<10$^{-4}$) for super-solar C/O. Measuring C/O from CO alone would require a CO abundance more precisely derived than most data presently allow. Perhaps of greater interest, however, are the ratios of the various molecules as C/O changes. For example, for all but the smallest C/O, CO/H$_2$O should be greater than one. Only for low surface gravity (<3.5) do the model fits from Section 4.4 result in N(CO) > N(H$_2$O) and, as gravity increases, the discrepancy between the predicted and observed CO and H$_2$O abundances grows. This may provide indirect evidence supporting low surface gravity for HR 8799 b.

6. SUMMARY AND CONCLUSIONS

A new K-band spectrum of HR 8799 b, with a spectral resolution of ~4000, was measured and simultaneous detections of water, carbon monoxide, and methane absorption lines were made. Identification of lines from each molecule is possible by eye and confirmed by cross-correlating the observed spectrum with absorption templates for each molecule. The abundance of each molecule was determined by a fitting procedure where the mole fractions are treated as free parameters in sequences of synthetic spectra. The ensemble of near-IR to thermal IR observations for HR 8799 b are best reproduced by an atmosphere with T$_{\text{eff}}$ = 1000, log(g) = 3.5. The log mole fractions are found to be between −3.09 and −3.91 for H$_2$O, between −3.30 and −3.72 for CO, and between −5.06 and −5.85 for CH$_4$. The best matching models have C/O between 0.55 and 0.7 depending heavily on log(g), as also found in K13, with C/O decreasing with increasing log(g). If the surface gravity is closer to log(g) = 4, as predicted by hot-start cooling tracks (Baraffe et al. 2003), then CO would be less abundant than H$_2$O (see Table 1) with a C/O ~ 0.4. Such a situation would require C and O abundances that deviate from those predicted by the Öberg et al. (2011) model, perhaps resulting from planetesimal accretion or core dredging.

A cross-correlation analysis of H-band data from B11, taken at a similar spectral resolution as the K-band data, revealed no methane signature. A detection of CH$_4$ absorption lines in the K-band but not in H may seem unexpected when compared to late-type brown dwarfs that often show more prominent CH$_4$ absorption in H than K. As shown here, the methane abundance in HR 8799 b is many orders of magnitude below that found in the atmospheres of field brown dwarfs, resulting in weaker methane absorption at all wavelengths. For photospheric temperatures and pressures appropriate for HR 8799 b, the average methane opacity (in units of cm$^2$/molecule) across K is about 10 times stronger than the average opacity across H, while the average water opacity is about 10 times stronger than methane in H and 10 times weaker than methane in K. Consequently, water opacity likely overwhelms that of methane across the H band. The characteristics of these opacity sources, combined with lower S/N in the H-band data, all contribute to the non-detection of methane in the H-band spectrum.

Low methane abundance in HR 8799 b is consistent with previous studies of non-equilibrium chemistry in hot, low gravity atmospheres. The mixing ratio of CH$_4$ in young giant exoplanets is, potentially, a useful probe of the vertical mixing. Using the inferred CH$_4$ abundance, the coefficient of eddy diffusion was found to be greater than 10$^6$ and very near 10$^7$ cm$^2$ s$^{-1}$ for the preferred T$_{\text{eff}}$ = 1000 K. These K$_d$ values are consistent with values appropriate for Jupiter’s deep troposphere (Visscher et al. 2010). Zahle & Marley (2014) explore the topic of non-equilibrium CH$_4$ in the context of young giant planets and their predictions are in good agreement with the values presented here.

HR 8799 b and c are the first exoplanets to have C/O ratios determined from spectroscopic data with high S/N and high spectral resolution (R ~ 4000). Young giant planets, still orbiting their star beyond the H$_2$O-frost line, provide important opportunities to study the link between formation and atmospheric chemistry. The C/O ratios of both HR 8799 b and c are similar and potentially super-stellar, but stellar values are not completely excluded. Refinements of C/O and individual molecular abundances will require improvements in the determination of surface gravity, independent of evolutionary models, perhaps with near-IR observations at even higher spectral resolution. Observations with the Hubble Space Telescope, at wavelengths within near-IR water absorption bands, might also help narrow the range of allowed abundances found here (A. Rajan et al. 2015, in preparation). However, comparisons to such data would face similar limitations as here, associate with effective temperature and gravity. More observations across the thermal infrared (3−5 μm), perhaps with future ground-based integral field spectrographs or with the James Webb Space Telescope, could provide complete coverage of strong CH$_4$, CO, and CO$_2$ absorption bands. New measurements across this wavelength range would also help improve effective temperature and gravity estimates. Model uncertainties need to be better understood as well, in particular, those associated with clouds and natural molecular line broadening.

There are now three young directly imaged planet-mass companions (HR 8799 b, c, and 2M1207B) that show evidence of disequilibrium chemistry in their deep troposphere. While three is too few to constitute a trend, the data and models suggest that chemical quenching is common among this class of exoplanet. For planets as warm as those orbiting HR 8799, the quenching likely occurs below the condensation depths and, consequently, bulk C/O ratios are inferable from their photospheric H$_2$O and CO abundances. Given the broad absorption features of these molecules, it may be possible to infer C/O for massive planets from the low-resolution spectra provided by GPI, P1640, and SPHERE.

We thank the referee, Thayne Currie, for useful comments and a careful review of this paper. We also thank Sergei Yurchenko and the ExoMol group for providing a copy of their methane line list in advance of publication. We also thank Peter Hauschildt, Isabelle Baraffe, Gilles Chabrier, and Mark Marley for fruitful discussions during the course of this work. The data presented herein were obtained at the W. M. Keck Observatory, operated as a scientific partnership among the California Institute of Technology, the University of California, and the National Aeronautics and Space Administration. The Observatory was made possible by the generous financial support of the
W. M. Keck Foundation. The authors wish to recognize and acknowledge the very significant cultural role and reverence that the summit of Mauna Kea has always had within the indigenous Hawaiian community. We are most fortunate to have the opportunity to conduct observations from this mountain. Most of the numerical work was carried out at the NASA Advanced Supercomputing facilities. This research was support by the NSF and NASA grants to LLNL and the University of Arizona. This research was also support by JPL/NexSci RSA awards. We thank all of these institutions for their support.

REFERENCES

Allard, F., Hauschildt, P. H., Alexander, D. R., Tamanai, A., & Schweitzer, A. 2001, ApJ, 556, 357
Asplund, M., Grevesse, N., Sauval, A. J., & Scott, P. 2009, ARA&A, 47, 481
Baraffe, I., Chabrier, G., Barman, T. S., Allard, F., & Hauschildt, P. H. 2003, A&A, 402, 701
Barber, R. J., Tennyson, J., Harris, G. J., & Tolchenov, R. N. 2006, MNRAS, 368, 1087
Barman, T. S., Macintosh, B., Konopacky, Q. M., & Marois, C. 2011a, ApJ, 733, 65
Barman, T. S., Macintosh, B., Konopacky, Q. M., & Marois, C. 2011b, ApJL, 735, L39
Bowler, B. P., Liu, M. C., Dupuy, T. J., & Cushing, M. C. 2010, ApJ, 723, 850
Currie, T., Burrows, A., Girard, J. H., et al. 2014, ApJ, 795, 133
Currie, T., Burrows, A., Itoh, Y., et al. 2011, ApJ, 729, 128
Esposito, S., Mesa, D., Skemer, A., et al. 2013, A&A, 549, A52
Fabrycky, D. C., & Murray-Clay, R. A. 2010, ApJ, 710, 1408
Fegley, B., Jr., & Lodders, K. 1994, Icar, 110, 117
Galicher, R., Marois, C., Macintosh, B., Barman, T., & Konopacky, Q. 2011, ApJL, 739, L41
Goorvitch, D. 1994, ApJS, 95, 535
Helled, R., & Schubert, G. 2009, ApJ, 697, 1256
Hinz, P. M., Rodigas, T. J., Kenworthy, M. A., et al. 2010, ApJ, 716, 417
Ingraham, P., Marley, M. S., Saumon, D., et al. 2014, ApJL, 794, L15
Karkoschka, E., & Tomasko, M. G. 2010, Icar, 205, 674
Konopacky, Q. M., Barman, T. S., Macintosh, B. A., & Marois, C. 2013, Sci, 339, 1398
Krabbe, A., Gasaway, T., Song, L., et al. 2004, Proc. SPIE, 5492, 1403
Larkin, J., Barczys, M., Krabbe, A., et al. 2006, NewAR, 50, 362
Macintosh, B., Graham, J. R., Ingraham, P., et al. 2014, PNAS, 111, 12661
Marley, M. S., Saumon, D., Cushing, M., et al. 2012, ApJ, 754, 135
Marois, C., Macintosh, B., Barman, T., et al. 2008, Sci, 322, 1348
Marois, C., Zuckerman, B., Konopacky, Q. M., Macintosh, B., & Barman, T. 2010, Natur, 468, 1080
Metchev, S., Marois, C., & Zuckerman, B. 2009, ApJL, 705, L204
Metchev, S. A., Heinze, A., Apai, D., et al. 2015, ApJ, 799, 154
Öberg, K. I., Murray-Clay, R., & Bergin, E. A. 2011, ApJL, 743, L16
Oppenheimer, B. R., Baranec, C., Beichman, C., et al. 2013, ApJ, 768, 24
Pueyo, L., Soummer, R., Hoffmann, J., et al. 2015, ApJ, 803, 31
Sadakane, K. 2006, PASJ, 58, 1023
Skemer, A. J., Hinz, P. M., Esposito, S., et al. 2012, ApJ, 753, 14
Smith, M. D. 1998, Icar, 132, 176
Visscher, C., & Fegley, B., Jr. 2005, ApJ, 623, 1221
Visscher, C., Moses, J. I., & Saslow, S. A. 2010, Icar, 209, 602
Warmbier, R., Schneider, R., Sharma, A. R., et al. 2009, A&A, 495, 655
Wong, M. H., Mahaffy, P. R., Atreya, S. K., Niemann, H. B., & Owen, T. C. 2004, Icar, 171, 153
Yurchenko, S. N., & Tennyson, J. 2014, MNRAS, 440, 1649
Zahnle, K. J., & Marley, M. S. 2014, ApJ, 797, 41