A Near-infrared Chemical Inventory of the Atmosphere of 55 Cancri e

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Abstract

We present high-resolution near-infrared spectra taken during eight transits of 55 Cancri e, a nearby low-density super-Earth with a short orbital period (<18 hr). While this exoplanet’s bulk density indicates a possible atmosphere, one has not been detected definitively. Our analysis relies on the Doppler cross-correlation technique, which takes advantage of the high spectral resolution and broad wavelength coverage of our data, to search for the thousands of absorption features from hydrogen-, carbon-, and nitrogen-rich molecular species in the planetary atmosphere. Although we are unable to detect an atmosphere around 55 Cancri e, we do place strong constraints on the levels of HCN, NH3, and C2H2 that may be present. In particular, at a mean molecular weight of 5 amu, we can rule out the presence of HCN in the atmosphere down to a volume mixing ratio (VMR) of 0.02%, NH3 down to a VMR of 0.08%, and C2H2 down to a VMR of 1.0%. If the mean molecular weight is relaxed to 2 amu, we can rule out the presence of HCN, NH3, and C2H2 down to VMRs of 0.001%, 0.0025%, and 0.08%, respectively. Our results reduce the parameter space of possible atmospheres consistent with the analysis of Hubble Space Telescope/WFC3 observations by Tsiaras et al. and indicate that if 55 Cancri e harbors an atmosphere, it must have a high mean molecular weight or clouds.

1. Introduction

Over the past several years, our understanding of hot Jupiter atmospheres has expanded enormously. This is due in large part to high-precision observations of transiting exoplanets that have enabled the detection of atomic and molecular species and provided constraints on the atmospheric structures of several gas giants (see, e.g., Madhusudhan 2019 for a broad overview of previous detections).

In contrast, the atmospheric properties of lower-mass, super-Earth exoplanets remain largely unconstrained. Their shallower transit depths and smaller atmospheric scale heights produce weaker spectroscopic signals that are more challenging to detect given our current observational capabilities. However, these atmospheres are of great scientific interest: in particular, they are predicted to be extraordinarily diverse, potentially being rich in carbon, silicate, or water vapors (e.g., Schaefer & Fegley 2009; Miguel et al. 2011; Hu & Seager 2014). Their atmospheric compositions are likely to reflect the varied formation and evolutionary histories that exoplanets in the super-Earth regime have experienced (e.g., Madhusudhan et al. 2016) and can shed light on these otherwise-elusive worlds.

A super-Earth of particular interest is the nearby transiting planet 55 Cancri e (hereafter referred to as 55 Cnc e), the existence of which was first suggested by McArthur et al. (2004). Dawson & Fabrycky (2010) later determined that its initially derived period of 2.808 days was an alias of its true, much shorter period of ~18 hr; this value was recently refined by Bourrier et al. (2018). 55 Cnc e has a mass of ~8M⊕ and radius of ~2R⊕ (Crida et al. 2018). It orbits a bright (V = 5.95; von Braun et al. 2011) GBV host star. The ultrashort orbital period of 55 Cnc e results in an equilibrium temperature in excess of 2000 K (e.g., Demory et al. 2016b), potentially leading to exotic atmospheric properties.

While the planet’s bulk density indicates that it could harbor an atmosphere (see, e.g., Gillon et al. 2012; Bourrier et al. 2018), several observational attempts have not been able to definitely detect its presence. In particular, Ehrenreich et al. (2012) found no evidence for an extended hydrogen atmosphere, and Esteves et al. (2017) and Jindal et al. (2020) derived limits on water absorption consistent with the exoplanet having either a hydrogen-poor atmosphere or a hydrogen-rich atmosphere that is significantly depleted in water vapor. Demory et al. (2016b) measured the photometric phase curve of 55 Cnc e at 4.5 μm with the Spitzer Space Telescope, finding a large temperature contrast between the exoplanet’s permanent day and night sides and a hot spot on the dayside offset by 40° from the substellar point.

Using grism spectroscopy data from the Wide Field Camera 3 (WFC3) on board the Hubble Space Telescope (HST), Tsiaras et al. (2016) reported the detection of an atmosphere around 55 Cnc e and suggested that it is likely hydrogen-rich, with a large scale height and high C/O ratio. They indicate that HCN is the most likely molecular candidate able to explain features detected at 1.42 and 1.54 μm, but caution that additional observations over a broader wavelength range would help confirm the results.
Hammond & Pierrehumbert (2017) modeled the phase curve of 55 Cnc e using an atmospheric global circulation model and found that a 90%–10% mixture of H$_2$ and N$_2$ in the atmosphere with cloud-forming species such as SiO can well approximate the observed phase variations. However, a complementary analysis by Angelo & Hu (2017) found that the atmosphere is likely dominated by either CO or N$_2$ with minor abundances of H$_2$O or CO$_2$. More recently, Miguel (2019) explored the expected chemical composition of the atmosphere of 55 Cnc e and concluded that transmission spectra should show strong features of NH$_3$ and HCN at mid- to long-infrared wavelengths if the atmosphere is nitrogen-rich, as may be expected from the large day–night temperature contrast (Hammond & Pierrehumbert 2017).

In this paper, we present high-resolution spectroscopy of 55 Cnc e from 950 to 2350 nm, focusing in particular on absorption features in the near-infrared (NIR) due to HCN. We also investigate the presence of NH$_3$, C$_2$H$_2$, CO, CO$_2$, and H$_2$O at NIR wavelengths. Our search for HCN is informed by the observational results of Tsiaras et al. (2016), who suggested that HCN is present in the atmosphere at a high volume mixing ratio (VMR) with acceptable values as low as 10$^{-5}$. In addition, Zilinskas et al. (2020) explored plausible VMRs for the case of a nitrogen-dominated atmosphere (following Miguel 2019). They find that CO may be present at relatively high VMRs ($\sim$10$^{-4}$–2, their Figure 3) across a wide range of pressures and C/O ratios. The expected VMR of H$_2$O depends largely on the C/O ratio, while CO$_2$ is expected to have a VMR $\lesssim$10$^{-7.5}$ for all pressures and C/O ratios considered. C$_2$H$_2$ is only expected at VMRs $>10^{-8}$ for C/O $>2$; however, tentative results from Tsiaras et al. (2016) suggested that C$_2$H$_2$ may be present with a VMR as high as 10$^{-5}$ at C/O $\sim$1.1. Zilinskas et al. (2020) also note that if nitrogen is introduced into the system, the atmosphere will tend to form HCN even if hydrogen is only present in small amounts.

Our analysis takes advantage of two facets of our observations: first, the wide wavelength coverage of our data, which span thousands of absorption features of both water and various carbon- and nitrogen-rich molecules in the NIR; and second, the very high spectral resolving powers ($R \sim$80,000) of our observations, which allow us to individually resolve these thousands of absorption features. Combining these features allows us to increase our detection capabilities, shedding further light on the atmospheric composition of 55 Cnc e.

Our paper is structured as follows. In Section 2, we describe the eight nights of observations obtained for this exoplanet, and in Section 3, we summarize the data-reduction process for these observations. Our analysis and results are presented in Sections 4 and 5, and we discuss these results in Section 6. Our conclusions follow in Section 7, with additional details in the appendices.

### 2. Observations

We observed six transits of 55 Cnc e with the Calar Alto high-resolution search for M dwarfs with Exoearths with Near-infrared and optical Échelle Spectrographs (CARMENES; Quirrenbach et al. 2014) located at the Calar Alto Astronomical Observatory. In this paper we focus on the NIR channel, which spans the wavelength range 960–1710 nm.

The observations were taken with varying exposure times (see Table 1), and in general each observation covered one full transit of 55 Cnc e (the transit duration being approximately 1.6 hr). We note that the observations taken on Night 4 and Night 6 (hereafter N4 and N6, respectively) suffered from poor observing conditions and did not cover the full transit. For this reason, we chose to exclude these nights from our analysis. The spectral resolving power of the instrument in the NIR is nominally $\lesssim$80,000 (Quirrenbach et al. 2018).

We also observed four transits of 55 Cnc e with the SpectroPolarimètre Infra-Rouge (SPIRou; Artigau et al. 2014) located at the Canada–France–Hawai’i Telescope (CFHT). The wavelength coverage of the data is 950–2350 nm. The 2–3 hr observation period of each night covered one full transit of 55 Cnc e, for a total of four full transits. The spectral resolving power of the instrument is nominally $\sim$75,000 (Artigau et al. 2014).

In total, we observed eight full transits and two partial transits of 55 Cnc e. The two partial transits suffered from poor observing conditions and were excluded from further analysis; thus, this paper reports on our analysis of eight full transits. Each night also includes a baseline of out-of-transit data, which is used to assess the significance of our results (see Section 4.4). A summary of our observations can be found in Table 1, and a list of the parameters used in this analysis can be found in Table 2.

| Night | Date (UT) | Instrument/Telescope | Duration (hr) | Frames (In/Out)$^a$ | Exp. Time (s)$^b$ | Avg. S/N | Used in Analysis? |
|-------|-----------|----------------------|--------------|---------------------|------------------|----------|-----------------|
| 1     | 2016 Dec 26 | CARMENES/Calar Alto   | 11.6         | 363 (80/283)        | 33.9             | 91       | Y               |
| 2     | 2017 Nov 22 | CARMENES/Calar Alto   | 5.7          | 141 (55/86)         | 58.0             | 145      | Y               |
| 3     | 2017 Nov 24 | CARMENES/Calar Alto   | 5.8          | 115 (43/72)         | 87.8             | 157      | Y               |
| 4     | 2017 Dec 9  | CARMENES/Calar Alto   | 1.0          | 26 (9/16)           | 53.1             | 108      | N               |
| 5     | 2017 Dec 11 | CARMENES/Calar Alto   | 5.6          | 92 (45/47)          | 86.6             | 71       | Y               |
| 6     | 2017 Dec 17 | CARMENES/Calar Alto   | 5.5          | 59 (14/45)          | 87.9             | 74       | N               |
| 7     | 2019 Feb 14 | SPIRou/CFHT           | 2.6          | 77 (47/30)          | 94.7             | 268      | Y               |
| 8     | 2019 Feb 25 | SPIRou/CFHT           | 2.5          | 73 (47/26)          | 94.7             | 300      | Y               |
| 9     | 2019 Apr 17 | SPIRou/CFHT           | 2.7          | 54 (34/20)          | 94.7             | 247      | Y               |
| 10    | 2019 May 1  | SPIRou/CFHT           | 2.3          | 73 (46/27)          | 94.7             | 250      | Y               |

Notes.

$^a$ (In/Out) refers to the number of in- and out-of-transit frames for each night.

$^b$ The exposure times refer to the average exposure time across all observations for each night.
Table 2

Star and Planetary Parameters Used in This Analysis

| Parameter | Value | Reference |
|-----------|-------|-----------|
| Spectral type | K | von Braun et al. (2011) |
| J-band flux | 4.59 | Ducati (2002) |
| H-band flux | 4.14 | Ducati (2002) |
| K-band flux | 4.015 | Curri et al. (2003) |
| $T_{\text{eff}}$ (K) | 5172 | Yee et al. (2017) |
| log g | 4.43 | Yee et al. (2017) |
| [Fe/H] | 0.35 | Yee et al. (2017) |
| $R_\ast$ ($R_\odot$) | 0.980 | Crida et al. (2018) |
| $K$ (ms$^{-1}$) | 6.02 | Bourrier et al. (2018) |
| $m_p$ ($M_\odot$) | 8.59 | Crida et al. (2018) |
| $r_\ast$ ($R_\odot$) | 1.947 | Crida et al. (2018) |
| $V_{\text{sys}}$ (km s$^{-1}$) | 27.58 | Nidever et al. (2002) |
| Orbital period (days) | 0.7365474 | Bourrier et al. (2018) |
| Midtransit (JD) | 2457063.2096 | Bourrier et al. (2018) |
| Semimajor axis (au) | 0.01544 | Bourrier et al. (2018) |
| Inclination (degrees) | 83.59 | Bourrier et al. (2018) |
| $R_p/R_\ast$ | 0.0182 | Bourrier et al. (2018) |
| $w/R_\ast$ | 3.52 | Bourrier et al. (2018) |
| $\mu_1$ | 0.3156 | Claret (2004) |
| $\mu_2$ | 0.2893 | Claret (2004) |

Note.

* $K$; radial velocity semiamplitude.

3. Data Reduction

The raw data frames obtained using CARMENES were initially reduced by the observatory with the CARMENES reduction pipeline CARACAL (Caballero et al. 2016), while the data obtained using SPIRou were extracted by the observatory using the SPIRou Data Reduction Software (DRS).\(^8\) Note that while the SPIRou DRS does include a telluric correction, we have chosen to carry out this correction ourselves (see Section 3.1); the data products extracted from the SPIRou DRS are thus wavelength-corrected 2D spectra. Note as well that both pipelines supply a barycentric Earth radial velocity (BERV) correction. Examples of extracted spectra for both CARMENES and SPIRou are shown in the top left and top right panels of Figure 1, respectively, while all extracted and reduced spectra are shown in the first panels of the figures presented in Appendix A.

The next steps of our data-reduction process proceeded similarly to Deibert et al. (2019). We interpolated our data to a common wavelength grid with a linear interpolation. We then removed contaminating cosmic rays through median filtering, where points falling outside of a threshold of five median absolute deviations were flagged as outliers and masked during subsequent analyses.

To account for the grating-dependent variation in brightness at different spectral orders in the data (i.e., the “blaze function”), we carried out a blaze correction. Such a correction is necessary for observations taken using Échelle spectrographs. The effect was removed separately for each night and each individual order of the data. To do this, we divided the first science spectrum of each night (the “reference spectrum”) from all science spectra and fit this product with a low-order polynomial. The polynomial fit was then divided out of each individual observation. This removed the effects of the blaze response function, resulting in a normalized spectrum that could be used for subsequent analysis. The procedure additionally corrects for other wavelength-dependent variations such as air-mass effects or differential slit losses.

The results of these initial data-reduction steps on a single order of $N_2$ (the 24th order) and $N_3$ (the 30th order) can be seen in the second left and second right panels of Figure 1 for the CARMENES and SPIRou observations, respectively. Additionally, the results of applying these corrections to all nights and orders of both data sets are shown in the second panels of the figures presented in Appendix A.

3.1. Correction of Systematic Effects

After the initial reduction process described above, the resultant spectra were largely dominated by both stellar and telluric absorption lines, seen as vertical lines in, for example, the second left and second right panels of Figure 1. However, due to the essentially stationary nature of these lines when compared with absorption due to the exoplanet’s atmosphere (which varies in radial velocity from $\sim$60 km s$^{-1}$ to $\sim$+60 km s$^{-1}$ over the course of the transit), these features can be removed using the SYSREM algorithm, first described by Tamuz et al. (2005). SYSREM allows for linear, systematic effects that appear in many data sets of the same sample to be removed through an algorithm that, in the case of equal uncertainties, reduces to a principal component analysis (PCA) algorithm.

The correction was determined using both in- and out-of-transit frames, and each order of the data was treated separately. For all observations, the average air mass at each exposure was taken as an initial approximation of the systematic effects to be removed. For consistency, we chose to apply the same number of iterations of the algorithm to each order; to determine this number, we calculated the rms of the residuals after subsequent iterations of SYSREM. We found that on average, six iterations of the algorithm was the point at which the rms of the residuals had plateaued and additional applications of the algorithm did not yield a significant improvement. The third left and third right panels of Figure 1 show the results of applying six iterations of the SYSREM algorithm to CARMENES and SPIRou spectra, respectively. The results of applying six iterations to all nights and orders of each data set are shown in the figures in Appendix A.

The algorithm performs poorly around strong or closely spaced lines; in particular, several orders of our observations (i.e., those at the edges of the $Y$, $J$, $H$, and $K$ photometric bands) suffer from significant telluric absorption. These strong lines make the blaze response correction difficult, and as a result, nonlinear effects are introduced into the spectra that cannot be removed using SYSREM. To reduce contamination from these poorly constrained frames, we followed, for example, Snellen et al. (2010), Esteves et al. (2017), and Deibert et al. (2019) in weighting each frame and each pixel by its standard deviation (shown in the fourth panels of Figure 1, as well as the figures presented in Appendix A). This step reduces the contribution from the noisier portions of the data. Additionally, we have chosen to fully exclude several particularly contaminated orders (those located within the gaps between the $Y$, $J$, $H$, and $K$ bands) from further analysis. These are described in greater detail in Appendix A.

\(^8\) http://www.cfht.hawaii.edu/Instruments/SPIRou/SPIRou_pipeline.php
Although the use of SYSREM for the removal of telluric features is well established (see, e.g., the discussion in Birkby 2018), we repeated the telluric removal process for a subset of our observations and atmospheric models using Molecfit (Kausch et al. 2015; Smette et al. 2015), a tool originally developed for the European Southern Observatory (ESO) consortium that corrects
telluric absorption based on synthetic modeling of the Earth’s atmospheric transmission. Molecfit has recently been used on both high-resolution optical and NIR observations (e.g., Allart et al. 2017, 2018; Salz et al. 2018; Cabot et al. 2020; Seidel et al. 2020, among others).

Here, we largely followed the methods laid out in Allart et al. (2017) and Salz et al. (2018) to apply Molecfit to our own observations. We used version 2.0.1 of the software, which was the most recent version available at the time of our analysis. Following Salz et al. (2018), we used a high-resolution synthetic stellar spectrum (PHOENIX; Husser et al. 2013), matching the properties of 55 Cnc A ($T_{\text{eff}} \approx 5200$ K, $\log g \approx 4.5$ dex, approximately solar metallicity; Yee et al. 2017) in order to identify and mask stellar features in our spectra. We then checked these masked regions by eye and adjusted where necessary. Following this, we selected narrow regions containing intermediate-strength telluric lines (i.e., not saturated), few or no stellar lines, and a flat continuum distributed throughout our spectra to fit. The remaining regions of each spectrum were corrected with the Calctrans tool, which is used to apply fits from Molecfit to the rest of the data. Each individual spectrum was fit and corrected separately. The goodness-of-fits for our data are comparable to those obtained by Allart et al. (2017); in our case, the average $\chi^2$ across all fits is 10.9. We note that this somewhat large value can likely be explained by the fact that our fit does not include stellar lines. Examples of this correction can be seen in the fifth panels of Figure 1, while an example of the standard deviation of this correction across wavelength channels can be seen in the final panels of Figure 1.

Additional details on our fit results, as well as the parameters used for our fits, are presented in Appendix C.1. We discuss the efficacy of Molecfit compared to that of SYSREM in further detail in Section 6.2.

4. Analysis

Our analysis relies on the Doppler cross-correlation technique, which was used to obtain a robust atmospheric detection by Snellen et al. (2010). An overview of the work preceding Snellen et al. (2010), as well as the numerous detections made since then, is found in Birkby (2018). This technique requires high-resolution data in order to resolve individual absorption features from an atmospheric species, which are then cross-correlated with atmospheric models. The precision of the method increases with the number of lines included in the cross-correlation (e.g., Birkby 2018). That means molecules (which have rotation–vibration transitions that produce thousands of absorption lines) are ideal targets and are thus the focus of our analysis.

Following Snellen et al. (2010) and Deibert et al. (2019), among others, we Doppler-shifted our atmospheric models to a range of velocities and cross-correlated these with each frame of the data. We then phase-folded the correlations from the in-transit frames to a range of systemic velocities and summed over each velocity in order to obtain a grid of correlation strengths as a function of both systemic and Keplerian velocities. The grids were then summed over all relevant orders and all nights of our observations to increase the detection strength. An example of the analysis is shown in Figure 2, and the method is described in further detail in Section 4.2.

Note that we have only included orders for which the atmospheric model in question contains absorption features. Examples of these atmospheric models are displayed in Appendix B, and the models are described in further detail in the next section.

4.1. Atmospheric Models

Our analysis involves independently testing for the presence of various molecules (HCN, NH$_3$, C$_2$H$_2$, CO, CO$_2$, and H$_2$O) in the atmosphere of 55 Cnc e through cross-correlation with so-called “parametric models” similar to those used in Jindal et al. (2020). We explore a range of VMRs and mean molecular weights ($\mu$’s) of each of these molecules, described in further detail below. We note that these models are not self-consistent and are instead meant to provide us with an initial insight into the exoplanet’s atmosphere and the limitations of our method. Furthermore, various models (i.e., those with low mean molecular weights; see the top left panels of the figures in the following section) are nonphysical. Such models allow us to test our method, as they are easily recoverable by the model injection/recovery process (see Section 4.3). We describe the calculations of all models below.

4.1.1. Atmospheric Model Calculation

To constrain the VMRs and mean molecular weights ($\mu$’s) of HCN, NH$_3$, C$_2$H$_2$, CO, CO$_2$, and H$_2$O in the atmosphere of 55 Cnc e, we generated a set of models with varying VMRs and $\mu$’s for each of these compounds individually embedded in an inert H$_2$ atmosphere. The code used to generate these models is an updated version of the line-by-line, plane-parallel radiative transfer code used in, for example, Esteves et al. (2017) and Jindal et al. (2020).

Each model was generated on a wavelength grid spanning the full range of our observations, that is, between ~950 and 2500 nm with a velocity step size of 1 km s$^{-1}$. The model atmosphere was calculated across 50 atmospheric layers, and opacities were integrated along slanted paths from the direction of the star to the observer. Each model includes only a single molecule, and we assume a Voigt profile for the lines with a line wing cutoff of 100 cm$^{-1}$. The models were temperature-broadened using standard database parameters and included pressure-broadening coefficients from HITRAN (Gordon et al. 2017). The line strengths were adjusted for temperature at each layer. We assume that the VMR is constant throughout the atmosphere. In addition to molecular absorption, Rayleigh scattering and H$_2$–H$_2$ collision-induced absorption were also taken into account in all of our models (Borysow et al. 2001; Borysow 2002). As in Esteves et al. (2017) and Jindal et al. (2020), we account for the geometry during transit when performing the radiative transfer. Like Jindal et al. (2020), we adjust the radius at the bottom of the models iteratively in order to match, on average, the measured value of $R_p/R_\star$.

In the case of HCN, C$_2$H$_2$, and NH$_3$, we made use of the HITRAN line lists (Gordon et al. 2017). For CO, CO$_2$, and H$_2$O, we made use of the HITTEMP line lists (Rothman et al. 2010). As in Jindal et al. (2020), we make use of the full line lists for our models. We note that as some of these line lists are incomplete (e.g., the C$_2$H$_2$ line list), the shapes of various molecular bands in our models are not completely accurate; for example, several of the models presented in Appendix B show sharp cutoffs at both ends of their molecular bands.

To compare these models with our data, we convolved each of them to the resolution of our observations using a Gaussian
kernel. We then spline-interpolated to the same wavelength grid when calculating the cross-correlation function. Example models for each molecule are displayed in Appendix B.

### 4.2. Doppler Cross-correlation

For each night of observations, our data were cross-correlated with models at Doppler shifts spanning $-250 \text{ km s}^{-1}$ to $250 \text{ km s}^{-1}$, with 1 km s$^{-1}$ steps between each velocity. This is shown in the top left panels of Figure 2. Next, we phase-folded the correlation signal from the in-transit frames by shifting each correlation to the reference frame of 55 Cnc e. The in-transit frames were determined using a model light curve generated with the occultquad package from Mandel & Agol (2002). The parameters used for this model light curve, including limb-darkening parameters from Claret (2004), are summarized in Table 2. In order to account for the fact that the planetary radial velocity is not known with perfect precision, as well as to better understand the behavior of the cross-correlation function at velocities outside of the planetary rest frame (e.g., to investigate spurious correlation peaks due to residual telluric lines), we created a correlation map over a wide range of systemic velocities ($V_{\text{sys}}$) and planetary orbital velocities ($K_\text{p} \sin \omega \phi(t)$, where $\phi(t)$ is the orbital phase). We created the map for planetary RV semiamplitude ($K_\text{p}$) values ranging from 1 to 300 km s$^{-1}$, with a 0.5 km s$^{-1}$ step between each value. An example is shown in the bottom left panels of Figure 2.

For each model, these correlation grids were summed over orders containing significant molecular absorption, and then summed over all observations.

### 4.3. Model Injection and Recovery Tests

To assess the robustness of our pipeline and to place constraints on the atmospheric composition of 55 Cnc e, we performed injection and recovery tests for each model used in our analysis. The goal of these tests was to determine whether or not our data-reduction process, including the SYSREM algorithm, removes any signal that may be present, as well as to place sensitivity limits on our results.

We carried out these injection and recovery tests by multiplying the in-transit frames of each observation (prior to any data reduction past initial processing at the telescope) by an atmospheric model shifted to the frame of the exoplanet to create a synthetic “model + data” data set. Note that the model was only added to the in-transit frames of our data. This was done for each model described in Section 4.1, each order of every observation, and each night of observation. The synthetic “model + data” spectra were then processed through our data-reduction pipeline.
As a result, we were able to assess the sensitivity limits of our analysis, by determining which synthetic spectra were recovered by our pipeline. For example, the top left panel in Figure 3 shows results of injecting HCN models of various strengths into our data and repeating the Doppler cross-correlation process. In all panels, the black line represents the original data, and the magenta line represents the data with an atmospheric model injected (see Section 4.3). The volume mixing ratio and mean molecular weight of each model are indicated in the bottom right of the panel. The dark- and light-gray contours in each panel correspond to $1\sigma$ and $3\sigma$ confidence levels, respectively, and were calculated using the process described in Section 4.4. The data have been phase-folded and sliced at the orbital velocity of 55 Cnc e, $K_p \approx 231.4$ km s$^{-1}$. We are able to rule out atmospheric HCN at a mean molecular weight of 2 amu with a volume mixing ratio as low as 0.001%, and at a mean molecular weight of 5 amu with a volume mixing ratio as low as 0.02%. We note that any additional models that were analyzed but not displayed in this figure did not yield significant detections or limits.

Figure 3. Results of injecting HCN models of various strengths into our data and repeating the Doppler cross-correlation process. In all panels, the black line represents the original data, and the magenta line represents the data with an atmospheric model injected (see Section 4.3). The volume mixing ratio and mean molecular weight of each model are indicated in the bottom right of the panel. The dark- and light-gray contours in each panel correspond to $1\sigma$ and $3\sigma$ confidence levels, respectively, and were calculated using the process described in Section 4.4. The data have been phase-folded and sliced at the orbital velocity of 55 Cnc e, $K_p \approx 231.4$ km s$^{-1}$. We are able to rule out atmospheric HCN at a mean molecular weight of 2 amu with a volume mixing ratio as low as 0.001%, and at a mean molecular weight of 5 amu with a volume mixing ratio as low as 0.02%. We note that any additional models that were analyzed but not displayed in this figure did not yield significant detections or limits.

described in Section 3 and analyzed using the Doppler cross-correlation method described in Section 4.2. An example of the process is shown in the middle two panels of Figure 2.
a case where a correlation between a model atmosphere and the corresponding synthetic data set resulted in a detection (magenta line), whereas a correlation between that same model atmosphere and the true data set (black line) did not result in a detection. Likewise, the top right panel in Figure 3 shows a case where neither a correlation between a model atmosphere and the corresponding synthetic data set (magenta line) nor the correlation between that same model atmosphere and the true data set (black line) resulted in a detection. The model atmosphere in question (HCN with a VMR of 0.1% and a mean molecular weight of 10 amu) was beyond the sensitivity limits of our detection pipeline.

We note that various models with nonphysical, low mean molecular weights (e.g., the top left panel in Figure 8) allow us to confirm that the model injection/recovery process is working as expected. Such models are easily recovered by the injection/recovery process, as seen in the top left panels of the figures in the following section.

This model injection/recovery process thus allowed us to place constraints on both the atmospheric makeup of the exoplanet and the detection limits of our observations.

4.4. Detection Significance

In order to assess the significance of our results, we followed the methods described in Esteves et al. (2017) and Deibert et al. (2019). We derived 1σ and 3σ confidence levels for each feature in each night of the data by randomly selecting a set of out-of-transit frames corresponding to the number of in-transit frames for each night, assigning an in-transit phase to each of these spectra, and following through with the cross-correlation and phase-folding process as described in Section 4.2. We repeated this process 10,000 times, sorted the data, and then selected the 1σ and 3σ confidence levels based on the outcome. These levels were then compared to the correlation strengths of each model in order to assess their significance. An example is shown in the rightmost panel of Figure 2.

5. Results

In this section we present the results of applying the Doppler cross-correlation method, as described in Section 4.2, to our observations. As noted previously, we are searching for absorption features caused by the presence of atmospheric HCN, NH₃, C₂H₂, CO, CO₂, and H₂O. Note that the figures in the following sections show only a subset of the models we analyzed, and all additional models not displayed in the figures did not result in significant detections or limits. Note as well that we are probing a grid of mean molecular weights and VMRs, and various combinations result in models that are nonphysical. For example, a high (∼10%) VMR for CO₂ would result in a mean molecular weight higher than 2 amu. However, such models allow us to test our method and ensure that the injection/recovery process is working as expected.

5.1. Hydrogen Cyanide

Figure 3 shows the results of our search for HCN in the atmosphere of 55 Cnc e. Our aim was to further investigate the results of Tsiaras et al. (2016), who used HST/WFC3 observations to report the detection of an atmosphere and suggested that HCN is the most likely molecule able to account for the observed absorption features.

We analyzed a range of atmospheric models varying in VMR from 0.1% down to 5 × 10⁻⁵% and in mean molecular weight from 2 to 20 amu. Our model spectra were generated using HITRAN2016 (Gordon et al. 2017). We note that the results depend on the accuracy of the line list used, so future studies with updated line lists may yield different outcomes.

As seen in Figure 3, we can rule out the presence of HCN in the atmosphere of 55 Cnc e at a mean molecular weight of 2 amu with a VMR of 0.001%; if the mean molecular weight is increased to 5 amu, the lowest VMR that we can rule out is 0.02%.

5.2. Ammonia

Figure 4 shows the results of our search for NH₃ in the atmosphere of 55 Cnc e.

We analyzed a set of models ranging in VMR from 5% to 10⁻⁸% and mean molecular weight ranging from 2 amu to 20 amu.

As can be seen in Figure 4, we are able to rule NH₃ out of the atmosphere at a mean molecular weight of 2 amu with a VMR as low as 0.0025%; if the mean molecular weight is increased to 5 amu, we can still rule NH₃ out with a VMR as low as 0.08%.

5.3. Acetylene

Figure 5 shows the results of our search for C₂H₂ in the atmosphere of 55 Cnc e.

We analyzed a set of models ranging in VMR from 20% to 10⁻⁸% and mean molecular weight ranging from 2 amu to 20 amu.

As can be seen in Figure 5, we are able to rule C₂H₂ out of the atmosphere of 55 Cnc e at a mean molecular weight of 2 amu with a VMR as low as 0.08%, and at a mean molecular weight of 5 amu with a VMR as low as 1.0%.

5.4. Carbon Monoxide

The results of our search for CO in the atmosphere of 55 Cnc e are summarized in Figure 6.

We analyzed a range of atmospheric models varying in VMR from 10% down to 10⁻⁶% and in mean molecular weight from 2 to 30 amu.

As shown in Figure 6, we are unable to detect atmospheric CO in our data. However, we are able to tentatively rule out the possibility of CO being present in the atmosphere of 55 Cnc e at a mean molecular weight of 2 amu and a VMR as low as 1.0% at the 3σ level. Note, however, that there are numerous additional features with peaks >1σ that are likely due to noise in the data (see, e.g., the discussion in Esteves et al. 2017, who noticed a similar phenomenon for optical transit data of 55 Cnc e). For this reason, we caution that our limits on the presence of CO are only tentative and warrant further investigation.

5.5. Carbon Dioxide

The results of our search for CO₂ in the atmosphere of 55 Cnc e are summarized in Figure 7.

As was the case with CO (see Section 5.4), we analyzed a range of atmospheric models varying in VMR from 10% down to 10⁻⁶% and in mean molecular weight from 2 to 30 amu.

As can be seen in Figure 7, we are neither able to detect atmospheric CO₂ in our data nor place any significant constraints on its presence. We note that while a peak is present in the
injected data at a systemic velocity of $0 \text{ km s}^{-1}$ and the orbital velocity of 55 Cnc e, as would be expected for a detection, it does not surpass $3\sigma$ and therefore is not sufficiently significant to make any conclusions about the presence or lack of atmospheric CO$_2$.

5.6. Water

The results of our search for H$_2$O in the atmosphere of 55 Cnc e are summarized in Figure 8.
We analyzed a range of atmospheric models varying in VMR from 20% down to $10^{-8}$% and in mean molecular weight from 2 to 20 amu.

As was the case with CO$_2$ (see Section 5.5), none of the injected models seen in Figure 8 surpass the $3\sigma$ confidence level, and thus we are unable to place any limits on the presence of H$_2$O in the atmosphere of 55 Cnc c with these data alone. This is likely due to the imperfect removal of telluric water lines in the data (see Section 3.1 and the additional discussion in Section 6.2 and Appendix D for further details).

Figure 5. Results of injecting C$_2$H$_2$ models of various strengths into our data and repeating the Doppler cross-correlation process. The panels are as described in the caption of Figure 3. We are able to rule C$_2$H$_2$ out of the atmosphere of 55 Cnc c at a mean molecular weight of 2 amu with a volume mixing ratio as low as 0.08%, and at a mean molecular weight of 5 amu with a volume mixing ratio as low as 1.0%. We note that any additional models with lower VMRs or higher mean molecular weights that were analyzed but not displayed in this figure did not yield significant detections or limits.
Figure 6. Results of injecting CO models of various strengths into our data and repeating the Doppler cross-correlation process. The panels are as described in the caption of Figure 3. We are able to tentatively rule out the presence of CO in the atmosphere of 55 Cnc e at a mean molecular weight of 2 amu down to a volume mixing ratio of 1.0% at a confidence of 3σ, as can be seen in the top two panels on the left. However, we caution that there are many additional peaks surpassing 1σ in the results (likely due to noise in the data) and that this may have affected our model injection/recovery process.

Figure 7. Results of injecting CO₂ models of various strengths into our data and repeating the Doppler cross-correlation process. The figures are as described in the caption of Figure 3. As neither the data (black lines) nor the data with models injected (magenta lines) surpass the 3σ confidence levels, we have neither detected nor can place limits on the presence of CO₂ in the atmosphere of 55 Cnc e.
6. Discussion

6.1. Comparison with Tsiaras et al. (2016)

Our model injection/recovery tests for HCN (see Figure 3) significantly narrow the parameter space of potential atmospheres that are consistent with the results reported in Tsiaras et al. (2016). These authors sampled VMRs from $1 \times 10^{-8}$ to 10 amu and mean molecular weights from 2 to 10 amu. Their analysis indicates that the mean molecular weight of the atmosphere peaks at roughly 4 amu, with higher values being unlikely. Furthermore, strong absorption seen near 1.4 and 1.6 μm in their analysis indicates that the mean molecular weight is relatively low. They also reported that (of the molecules considered in their fit) HCN is the most likely absorber able to explain their observed absorption features, and that a scenario with a high VMR for HCN is favored, though values as low as 0.001% are acceptable.

While our results do rule out the most likely scenarios considered by Tsiaras et al. (2016), they are not in complete disagreement. A mean molecular weight of 2 amu at VMRs consistent with the Tsiaras et al. (2016) analysis is ruled out by our observations; however, it is possible that the mean molecular weight is slightly greater (~4 or 5 amu) and that the VMR is between 0.02% and 0.001%. If the detection in Tsiaras et al. (2016) is real, a higher mean molecular weight would be unlikely, since that would significantly mute the features in the transmission spectrum.

While additional observations will be necessary to determine whether a scenario with low VMR and high mean molecular weight can be ruled out completely, our analysis has provided significantly improved constraints on the presence of HCN and vastly decreased the parameter space of possible atmospheres. Our analysis has also provided constraints on the presence of NH₃ and C₂H₂ and suggests that if any of these three molecules are indeed present in the atmosphere of 55 Cnc e, they are likely to have high mean molecular weights, low VMRs, or both. We note that previous observations (e.g., Ehrenreich et al. 2012; Demory et al. 2016b) do support an atmosphere with high mean molecular weight.

Finally, we caution that these constraints rely on the accuracy of the line lists used to generate our models, and future updates to these line lists could yield different results. The issue has been discussed in detail in a number of previous studies. In the case of TiO, for example, Hoeijmakers et al. (2015) demonstrated that inaccurate line lists can hamper high-resolution retrievals. Likewise, Webb et al. (2020) observed absorption due to H₂O in high-resolution VLT/CRIRES spectra of HD 179949 b, but found a weak dependence on the line list used for the cross-correlation. Updates to the available line lists for each of the molecules used in this analysis could similarly impact our detection capabilities, and we therefore note that the particulars of line lists should be kept in mind when interpreting our results.

6.2. Comparison with High-resolution Optical Spectroscopy

We note that previous studies (Esteves et al. 2017; Jindal et al. 2020) have been able to place significant constraints on the presence of H₂O in the atmosphere of 55 Cnc e using high-resolution spectra at optical wavelengths. In particular, recent work by Jindal et al. (2020) resulted in a 3σ lower limit of 15 amu on the mean molecular weight of 55 Cnc e’s atmosphere.
assuming it is water-rich (i.e., has a VMR > 0.1%) and that it does not have thick clouds. Our observations do not improve on these constraints.

Given the fact that the NIR wavelength ranges of CARMENES and SPIRou contain more absorption lines due to H$_2$O than the optical wavelength ranges of these previous works (e.g., compare our Figure 28 with Figure 8 of Esteves et al. 2017 and Figure 2 of Jindal et al. 2020), it could be expected that our data (which cover the same number of transits as Jindal et al. 2020) should give the same or even better constraints than those analyses. To investigate the discrepancy, we carried out a number of tests designed to probe the limits of our technique in the context of NIR H$_2$O (and CO$_2$) absorption. The full details of these tests are presented in Appendix D.

We conclude that the discrepancies between this work and Esteves et al. (2017) and Jindal et al. (2020) are largely due to our inability to fully remove telluric water features from our data. While the overall wavelength coverage of the observations used in this work is indeed broader than that of Jindal et al. (2020), and therefore contains a greater number of absorption lines due to H$_2$O, the telluric contamination at these redder wavelengths is far more severe than at the wavelengths considered in Jindal et al. (2020). As the individual absorption lines due to the exoplanet’s atmosphere are weak, our method relies heavily on our ability to combine the signals from many absorption lines, which in turn relies on our ability to remove telluric contamination adequately in the regions where these lines are present. SYSREM is less efficient in regions of strong telluric contamination; this can be seen in a comparison between the residuals after applying SYSREM in Jindal et al. (2020) and those in this work (see the plots in Appendix A). While additional iterations of SYSREM may aid in removing some residual telluric contamination, we show in Appendix D that additional iterations may also begin to remove the model itself and thus will not improve our detection capabilities. We also note that the signal-to-noise raitos ($S/NS$) of our observations (see Table 1) are in some cases significantly lower than those of Jindal et al. (2020), which would limit our sensitivities further.

As mentioned in Section 3.1.1, we also tried correcting for telluric absorption using Molecfit. We applied Molecfit and Ccalcit and Molecfit to every spectrum in each night of our CARMENES and SPIRou data. We then injected an atmospheric H$_2$O model with a VMR of 20% and a mean molecular weight of 2 amu into our data. In the first case, we have corrected telluric absorption using SYSREM (Section 3.1); in the second case, we have corrected telluric absorption using Molecfit and corrected stellar absorption using a mean stellar line template; in the third case, we have corrected telluric absorption using Molecfit and corrected stellar absorption using two iterations of SYSREM; and in the fourth case, we have injected the injected model at 100× its nominal strength into a single night of data and corrected for telluric absorption using Molecfit and stellar absorption using two iterations of SYSREM. In all cases, the correction is followed by the Doppler cross-correlation process as described in Section 4.2. A peak is visible in the cross-correlation at the expected location for SYSREM and Molecfit with a model injected at 100× its nominal strength; in the cases where Molecfit is used on the model at 1× its nominal strength, however, we are unable to detect a peak in the cross-correlation. The expected location is indicated by white dotted lines in all panels.
When running Molecfit on our CARMENES data, however, no such peak is present. In the case of SPIRou, a peak is visible at the expected location, but this signal is weaker than the case where SYSREM was used instead (Figure 10).

As a final test of what might be impacting our ability to recover injected H$_2$O models, we followed Alonso-Floriano et al. (2019) and Sánchez-López et al. (2019) in separately analyzing individual bands of our observations. We separated the CARMENES data into the $Y$, $J$, and $H$ bands and separated the SPIRou data into the $Y$, $J$, $H$, and $K$ bands.

Figures 11 and 12 show these results for CARMENES and SPIRou, respectively. In both cases, the contribution to the signal comes almost exclusively from the $J$ band (and, to a lesser extent, the $H$ band). This suggests that although our observations span a wide wavelength range, only a small fraction of that wavelength range is contributing to our detection capabilities. The other water approaches $3\sigma$. When running Molecfit on our CARMENES data, however, no such peak is present. In the case of SPIRou, a peak is visible at the expected location, but this signal is weaker than the case where SYSREM was used instead (Figure 10).

Figures 10 and 11. Comparison of our phase-folded SPIRou results for cases where telluric correction is carried out using SYSREM (left) and Molecfit (right). In both cases, we have injected an atmospheric H$_2$O model with a VMR of 20% and a mean molecular weight of 2 amu. In the panel on the right, stellar absorption has been corrected with two iterations of SYSREM. In this case, we see that the injected model is recovered when the data are corrected with Molecfit; however, the recovered signal is not as strong as in the case where the data are corrected with SYSREM.

Figure 11. Results of our model injection/recovery process (see Section 4.3) for the $Y$, $J$, and $H$ bands of our CARMENES observations. These tests use a water model with a VMR of 20% and a mean molecular weight of 2 amu (Figure 28). The primary plot shows $\sigma$ as a function of wavelength for the full wavelength range, and the insets show the phase-folded correlations for the data alone (top insets) and the data with a model injected (bottom insets). The insets are as described in the caption of Figure 2. The band is indicated in the title of each inset, and the corresponding region is marked in the primary plot. The white dotted lines show the expected location of the correlation signal. We see that the majority of the recovered signal comes from the $J$ band.
features present (see Figure 28) were likely not readily recovered by our model injection/recovery tests because they are comparatively weaker and because SYSREM was not able to remove telluric features completely in these regions (see the figures in Appendix A, particularly the bottom two panels of each).

We also ran the individual band analysis on our strongest HCN model as a comparison. The results are shown in Figures 13 and 14 for CARMENES and SPIRou, respectively. In this case, we see that a signal is recovered in all bands except the K band. For CARMENES the signal is strongest in the Y and H bands, whereas for SPIRou the signal is noticeably strongest in the J and H bands.

6.3. A Nitrogen-dominated Atmosphere?

Several previous studies have pointed to a nitrogen-dominated atmosphere for 55 Cnc e. Hammond & Pierrehumbert (2017) used 3D calculations to show that the offset observed in the phase curve (Demory et al. 2016b; Angelo & Hu 2017), as well as the large day–night temperature contrast, may be explained by an N-dominated atmosphere. The analysis by Miguel (2019) also supports this scenario. To this end, Miguel (2019) explored the observable features in the spectra of an N-dominated atmosphere for 55 Cnc e. Through analytical arguments, equilibrium chemistry calculations, and adopting
Titan’s elemental abundances as a potential composition, Miguel (2019) showed that although N₂ is expected to be the most abundant molecule in the atmosphere (followed by H₂ and CO), the transmission spectra should show strong features of NH₃ and HCN. However, a decrease in the N/O ratio would tend to weaken these NH₃ and HCN features.

The transmission spectra calculated in Miguel (2019, their Figure 3, right panel) range between 3 and 20 μm and are thus outside the range of our own observations. Figures 6 and 7 of Miguel (2019) show the mixing fraction of the most abundant observable molecules as a function of temperature at a pressure of ∼1.4 bar (as calculated by Angelo & Hu 2017) and the mixing fractions as a function of pressure at different N/O ratios, respectively. For all temperatures considered by Miguel (2019) at a pressure of ∼1.4 bar, the VMR of NH₃ is less than ∼10⁻⁴%, while at all pressures considered and for all N/O ratios considered, the VMR of NH₃ is less than ∼10⁻⁵%. Our analysis rules out most low-mean-molecular-weight, high-VMR scenarios, which is consistent with expected VMRs from Miguel (2019) and with previous work that has combined mass and radius measurements with interior modeling to show that the atmosphere should have a high mean molecular weight (Demory et al. 2011; Winn et al. 2011; Bourrier et al. 2018).

6.4. A Cloudy Atmosphere?

We note that the limits we have placed throughout this section assume that any signals present in the atmosphere are not obscured by clouds or hazes. However, the presence of clouds or hazes could act to obscure atmospheric signals, limiting our ability to make detections. Therefore, our results may also be consistent with a cloudy atmosphere. The limits we have placed throughout this analysis are only relevant in the case of a cloud-free atmosphere, as the models were injected into the data under the assumption that they were not obscured at any altitude by clouds or hazes. We note as well that various other investigations into the composition of 55 Cancri e’s atmosphere (Tsiaras et al. 2016; Esteves et al. 2017; Jindal et al. 2020) made similar assumptions, meaning that those limits also pertain to the case in which 55 Cancri e does not harbor clouds.

While an in-depth exploration of the effects of clouds or hazes on the atmosphere could prove insightful, such an analysis is beyond the scope of this work. However, we note that an analysis by Mahapatra et al. (2017) found that despite 55 Cancri e’s high equilibrium temperature (∼2400 K, Demory et al. 2016a), conditions on 55 Cancri e may allow for mineral clouds to form. Such cloud formation is likely only possible in a thin atmospheric region and requires strong vertical replenishment (Mahapatra et al. 2017). Hammond & Pierrehumbert (2017) also investigated the possibility of clouds and found that given the observed high equilibrium temperature and a range of partial pressures from Miguel et al. (2011), Na is unlikely to condense and form clouds, whereas SiO could potentially condense on the planet’s nightside (both Na and SiO could arise from a dayside magma ocean; e.g., Schaefer & Fegley 2010; Miguel et al. 2011; Hammond & Pierrehumbert 2017).

6.5. Refraction

Briefly, we note that while the effects of refraction were not considered in our model atmosphere calculations (see Section 4.1), it has been shown that refraction can act to mute spectral features in the lower atmosphere by creating a gray continuum similar to that produced by optically thick clouds (Bétrémieux & Swain 2018). For thin atmospheres around terrestrial exoplanets, the largest pressure that can be probed may indeed be the exoplanet’s surface pressure; with increasingly thicker atmospheres, however, refraction may prevent observations of the lower atmosphere.

Bétrémieux & Swain (2018) calculate the refractive boundaries of several hot Jupiters and terrestrial exoplanets for various atmospheric compositions in order to assess the impact of refraction on observations. In most cases, these refractive boundaries are located at pressures >1 bar.

In the case of 55 Cancri e, which has a high equilibrium temperature (∼2400 K, Demory et al. 2016a), and the observations and models presented in this paper, refraction should not have a large effect on our results. However, future work (particularly of observations that probe deeper into the atmosphere) may benefit from including the effects of refraction in model calculations.

7. Conclusion

We have presented our analysis of high-resolution NIR transmission spectroscopy of the transiting super-Earth 55 Cancri e.
This paper shows the results of the Doppler cross-correlation technique, which takes advantage of the large change in radial velocity of the exoplanet during its transit as well as the high spectral resolution of our observations, allowing us to resolve individual molecular features and disentangle the planetary signal from stellar and telluric absorption lines.

In the cases of atmospheric HCN, NH$_3$, and C$_2$H$_2$, we are able to place strong upper limits. We can rule HCN out of the atmosphere of 55 Cnc e at a VMR as low as 0.001% with a mean molecular weight of 2 amu; if the mean molecular weight is increased to 5 amu, we can rule HCN out down to a VMR of 0.02%. Our findings rule out the most likely models suggested by the analysis of Tsiaras et al. (2016), but several models remain with lower VMRs and a mean molecular weight of ~4 or 5 amu that are both consistent with the Tsiaras et al. (2016) analysis and are not ruled out by our observations.

We can rule NH$_3$ out of the atmosphere at a VMR as low as 0.0025% if the mean molecular weight is 2 amu; if it is increased to 5 amu, we can rule NH$_3$ out down to a VMR of 0.08%. Recent work suggests that the atmosphere of 55 Cnc e is likely N-dominated (Angelo & Hu 2017; Hammond & Pierrehumbert 2017). Moreover, Miguel (2019) showed that both NH$_3$ and HCN should be present in an N-dominated atmosphere and that transmission spectra from 3 to 20 μm should show strong features of NH$_3$ and HCN. Our results rule out low-mean-molecular-weight, high-VMR scenarios for both molecules; however, they are consistent with calculations suggesting that the atmosphere should have a high mean molecular weight, and thus with the conclusions of Miguel (2019).

Finally, we can rule C$_2$H$_2$ out of the atmosphere at a VMR as low as 0.08% if the mean molecular weight is 2 amu; if the mean molecular weight is increased to 5 amu, we can rule C$_2$H$_2$ out of the atmosphere down to a VMR of 1.0%.

In the case of atmospheric CO, CO$_2$, and H$_2$O, on the other hand, we are unable to place significant constraints. We note that while the injections of CO models with a VMR of either 10% or 1% and a mean molecular weight of 2 amu do result in >3σ detections, there are many additional features in the data at >1σ, and we thus caution that the peaks seen at >3σ in Figure 6 should be treated as tentative and warrant further investigation.

Through several tests designed to probe the limits of our detection capabilities, we conclude that our inability to recover injected H$_2$O and CO$_2$ models stems from the difficulty of removing telluric absorption lines across the broad NIR wavelength range of our data. Future analyses would benefit from exploring additional avenues of telluric correction.

While we do not detect an atmosphere around 55 Cnc e, we do provide improved constraints on the possible scenarios for one that may exist. Furthermore, we have demonstrated the efficacy of the Doppler cross-correlation method at detecting nitrogen-rich molecules in particular, which will be of use in future studies of super-Earth atmospheres. Our understanding of the nature of 55 Cnc e’s atmosphere is likely to advance in the coming years, thanks to the increased wavelength coverage of upcoming spectrographs that extend further into the infrared, improved telluric absorption removal techniques, and the launch of the James Webb Space Telescope.

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Software: astropy (Astropy Collaboration et al. 2013; Price-Whelan et al. 2018), Numpy (Harris et al. 2020), CARACAL (Caballero et al. 2016), Molecfit (Smette et al. 2015; Kausch et al. 2015), occultquad (Mandel & Agol 2002), Matplotlib (Hunter 2007), SciPy (Virtanen et al. 2020), IPython (Perez & Granger 2007).

Appendix A

Data Reduction

The full data-reduction process for each night and each order of our observations is presented here. The process is described in Section 3, and examples of the process being applied to specific orders of the CARMENES and SPIRou data sets are shown in the left and right panels of Figure 1, respectively. The orders containing significant telluric contamination (i.e., those between the standard photometric bands) were excluded from further analysis and are indicated by a gray scale in the figures.

A.1. CARMENES

Figures 15–18 show the results of applying the full data-reduction process to the four nights of CARMENES observations used in this analysis. We chose to exclude several orders from all further analyses due to severe telluric contamination that prevented the blaze correction or the SYSREM algorithm from being able to provide an adequate reduction; these are seen in regions where the standard deviation is much higher than the rest of the spectrum. Note that we also chose to exclude N$_4$ and N$_6$ from our analysis because of poor observing conditions (see Table 1).

A.2. SPIRou

Figures 19–22 show the results of applying the full data-reduction process to the four nights of SPIRou observations. Again, we have excluded regions of severe telluric contamination from our analysis and indicated these in gray scale.
Figure 15. Data-reduction process as applied to the first night of CARMENES observations (N1 in Table 1). The top panels show the data after they have been extracted from and reduced by the telescope, the second panels show the data after applying a blaze-correction and median-filtering algorithm (as described in Section 3), the third panels show the data after applying six iterations of the SYSREM algorithm (see Section 3.1), and the fourth panels show the standard deviation along each wavelength channel after applying the SYSREM algorithm.

Figure 16. Data-reduction process as applied to the second night of CARMENES observations (N2 in Table 1). The panels are as described in the caption of Figure 15.

Figure 17. Data-reduction process as applied to the third night of CARMENES observations (N3 in Table 1). The panels are as described in the caption of Figure 15.
Figure 18. Data-reduction process as applied to the fifth night of CARMENES observations (N5 in Table 1). The panels are as described in the caption of Figure 15. We note that SYSREM performed poorly in many orders, as seen in the third and fourth panels of the plot; however, we have chosen to keep these observations in our analysis. As described in Section 4, we weight each wavelength channel by its standard deviation, and thus we ensure that the areas where SYSREM performed poorly do not negatively impact our results.

Figure 19. Data-reduction process as applied to the first night of SPIRou observations (N7 in Table 1). The panels are as described in the caption of Figure 15.

Figure 20. Data-reduction process as applied to the second night of SPIRou observations (N8 in Table 1). The panels are as described in the caption of Figure 15.
Appendix B

Models

In this section we present example models for each molecule considered in our analysis (HCN, NH₃, C₂H₂, CO, CO₂, and H₂O; Figures 23–28, respectively). Further details on these models, including a description of how they were generated, are available in Section 4.1. Each example model shown here corresponds to the top left model of each plot in Section 5; see Figures 3–8.

For some of the models presented in this work (e.g., the C₂H₂ model in Figure 25), the line lists that are currently available are incomplete. This results in the sharp cutoffs in wavelength visible in numerous bands. Going forward, we expect that more complete and accurate line list data will become available, which would allow for a more complete and realistic model to be calculated.
Figure 23. Example HCN model calculated for 55 Cnc e with a mean molecular weight of 2 amu and a volume mixing ratio of 0.1%. This model is ruled out of the atmosphere, as seen in the top left panel of Figure 3.

Figure 24. Example NH$_3$ model calculated for 55 Cnc e with a mean molecular weight of 2 amu and a volume mixing ratio of 5.0%. This model is ruled out of the atmosphere, as seen in the top left panel of Figure 4.

Figure 25. Example C$_2$H$_2$ model calculated for 55 Cnc e with a mean molecular weight of 2 amu and a volume mixing ratio of 20%. This model is ruled out of the atmosphere, as seen in the top left panel of Figure 5.
Figure 26. Example CO model calculated for 55 Cnc e with a mean molecular weight of 2 amu and a volume mixing ratio of 10%. This model is tentatively ruled out of the atmosphere, as seen in the top left panel of Figure 6. We caution that this result is only tentative, as there are numerous additional peaks at $>1\sigma$ in our results.

Figure 27. Example CO$_2$ model calculated for 55 Cnc e with a mean molecular weight of 2 amu and a volume mixing ratio of 10%. This model corresponds to the phase-folded cross-correlations shown in the top left panel of Figure 7 and is not ruled out of the planet's atmosphere by our analysis.

Figure 28. Example H$_2$O model calculated for 55 Cnc e with a mean molecular weight of 2 amu and a volume mixing ratio of 20%. This model corresponds to the phase-folded correlations shown in the top left panel of Figure 8 and is not ruled out of the planet's atmosphere by our analysis.
Appendix C

Molecfit

In this section, we present additional details on our telluric-feature removal process using Molecfit. Although our analysis removes telluric features through the use of the SYSREM algorithm, we decided to compare our results with Molecfit in order to determine whether the removal of telluric features was limiting our ability to recover certain injected models (see Section 5.6 for further details). We largely followed the methods laid out in Allart et al. (2017) and Salz et al. (2018) to apply Molecfit to our observations.

C.1. Fit Parameters

The initial parameters used with Molecfit for every night are shown in Table 3. Further details on these parameters are available in Smette et al. (2015) and Kausch et al. (2015). We allowed Molecfit to fit for a Gaussian kernel that varies with wavelength and included fitting for the wavelength solution.

| Initial Parameters | Value | Notes |
|--------------------|-------|-------|
| ftol               | $10^{-10}$ | Relative $\chi^2$ convergence criterion |
| xtol               | $10^{-10}$ | Relative parameter convergence criterion |
| Molecules          | H$_2$O, CO$_2$, O$_3$, CO, CH$_4$, O$_2$ | Molecules included in the fit |
| cont$_{\text{cont.}}$ | 2 | Degree of coefficients for continuum fit |
| $\lambda_3$       | 1 | Initial constant term for continuum fit |
| $\omega_{\text{Gaussian}}$ | 3.5 | Polynomial degree of the refined wavelength solution |
| Kernel size        | 15 | Initial value for FWHM of Gaussian in pixels |
|                    |      | Size of Gaussian kernel in FWHM |

Note. We allow Molecfit to fit for molecules with absorption features present in the wavelength range of our data (see Molecules row) and apply a second-degree Chebyshev polynomial fit to the wavelength solution ($\lambda_3$). The continuum (cont$_{\text{cont.}}$) is fit with a second-degree polynomial, and as the data are normalized, we set an initial constant term of 1 for the continuum, which is then refined through the fit. The instrumental profile is initially assumed to be a Gaussian with a FWHM of 3.5 pixels; however, this too is refined through the fit. Molecfit uses the Levenberg–Marquardt technique to quickly solve the least-squares problem (Smette et al. 2015); the $\chi^2$ convergence parameter (ftol) and the parameter convergence criterion (xtol) of the Levenberg–Marquardt technique are set to $10^{-10}$.

Appendix D

Assessing Our H$_2$O and CO$_2$ Retrieval Capabilities

In the following sections, we present several additional tests designed to evaluate our H$_2$O and CO$_2$ model recovery capabilities.

D.1. White Noise Test

To test whether residual noise left in the data after the application of the SYSREM algorithm was affecting our final result, we followed a method similar to that of Esteves et al. (2017) by simulating a pure white noise data set generated to match the rms of each wavelength channel after applying SYSREM (see, e.g., the bottom panels of the figures in Appendix A). We tried injecting both a model H$_2$O atmosphere and a model CO$_2$ atmosphere into this white noise data set and repeated our analysis routine as described in Section 4 for each model. This allowed us to assess whether the residual noise level in the data after applying the SYSREM algorithm was the limiting factor in being able to recover H$_2$O and CO$_2$ models.

The results of these white noise tests are shown in Figures 29 (H$_2$O) and 30 (CO$_2$) for the CARMENES data set, and Figures 31 (H$_2$O) and 32 (CO$_2$) for the SPIRou data set.

In all cases, we see that in a data set composed of pure white noise, we are unable to recover even the strongest H$_2$O and CO$_2$ models. This suggests that SYSREM did not adequately remove stellar and telluric contamination in the data, and that the data themselves are simply too noisy to allow us to place strong constraints on the presence of H$_2$O or CO$_2$ in the atmosphere of 55 Cnc e. We note that H$_2$O and CO$_2$ contain a significant number of lines throughout the broad wavelength coverage offered by CARMENES and SPIRou; while these lines can in theory improve the strength of our detections, there will also be corresponding H$_2$O and CO$_2$ lines present in this wavelength range in the Earth’s atmosphere that contaminate the data and pose a challenge to the SYSREM algorithm. Future analyses would benefit from exploring other avenues of telluric absorption line removal.

In the case of the SPIRou data, the shift in the wavelength solution of the data themselves is slightly larger than the systematic shift in the wavelength solution. For most orders, the shift in the fitted centroid of the cross-correlation function is on average 0.04 pixels. For each night, we found that two orders experienced a slightly larger shift (on the order of $\sim$1 pixel); however, these were orders that had previously been discarded from the data due to excessive telluric contamination.

In the case of the SPIRou data, the shift in the fitted centroid of the cross-correlation function for each order is on average...
Figure 29. White noise test for the CARMENES data, as described in Appendix D.1. The panel on the left shows the results of injecting an atmospheric H$_2$O model with a VMR of 20% and a mean molecular weight of 2 amu (i.e., the model shown in Figure 28) into our CARMENES data set and repeating the Doppler cross-correlation process. The data with the model injected is represented by the black line, while the dark- and light-gray contours represent 1σ and 3σ confidence levels, respectively (see Section 4.4). The panel on the right shows the results of injecting this same atmospheric model into a white noise data set as described in Appendix D.1. The model that has been injected into the white noise data set is closer to the 3σ confidence level than that injected into the data; however, in neither case were we able to confidently retrieve the injected model.

Figure 30. Same as Figure 29, but for a CO$_2$ model with a VMR of 10% and a mean molecular weight of 2 amu (i.e., the model shown in Figure 27). We were unable to confidently recover the injected model in the original data set (left) or the white noise data set (right), but we note that the injected model is closer to the 3σ confidence level in the white noise data set than in the original data set.

Figure 31. White noise test for the SPIRou data, as described in Appendix D.1. The panels are as described in the caption of Figure 29. Again, the model that has been injected into the white noise data set here does not pass the 3σ confidence level.
We do not find that any orders experience a significantly larger shift. In addition to the test described above, we also selected several individual telluric lines in each data set and fit these with a Gaussian, determining the centroid of each line by the Gaussian’s expected value $\mu$. For these individual lines, we also did not find a significant shift in the wavelength solution.

Finally, we note that our data-reduction procedure (described in Section 3) involves interpolating each frame to a common wavelength grid. Overall, we do not think that a shift in the wavelength solution impacted our final results, given that the shift measured by the methods described above is significantly less than one pixel and less than the widths of the absorption lines themselves.

### D.3. Varying SYSREM Iterations

In addition to the tests described in the preceding sections, we investigated whether applying different numbers of iterations of SYSREM affected our ability to recover injected models. While the methods we used to determine the optimal number of iterations were model-free (see Section 3.1), it is possible that SYSREM had begun to overfit the data and remove signal from the injected model (see, e.g., the discussion in Brogi 2014). For the purposes of this test, we again used the water model with a VMR of 20% and a mean molecular weight of 2 amu (i.e., the model shown in Figure 28) and the CO$_2$ model with a VMR of 10% and a mean molecular weight of 2 amu (i.e., the model shown in Figure 27), because these models should be the easiest to detect.

The results are shown in Figures 33 and 34. The noise level decreases with increasing numbers of iterations of SYSREM and appears to plateau at six iterations, as determined previously (see Section 3.1). However, Figure 33 also shows that the strength of the injected water model decreases slightly after five iterations of the algorithm: while the injected model after five iterations surpasses the 3$\sigma$ level, this is not the case for the injected model after six iterations. This indicates that the SYSREM algorithm has begun to remove signal contributed by the model itself. In the case of CO$_2$, however, we find that the model is more readily detected after six iterations.
Although this test demonstrates that varying the number of iterations of SYSREM can have an impact on our ability to recover an injected model, we have chosen not to change the number of iterations used in our analysis for several reasons. First, the number of iterations initially chosen was based on an average optimal result across all orders and was independent of the model or molecule being considered. We have chosen to implement a model-free method for determining the optimal number of iterations of SYSREM so that the specifics of the models being injected are less likely to impact our results.

We also note that the change in strength between five and six iterations as seen in Figure 33 is not highly significant: while the injected model after five iterations slightly surpasses the 3σ level, the injected model after six iterations is close to (but not quite at) the 3σ level. While it is possible that the number of iterations of SYSREM used in our analysis affected some of the results shown in Figure 8, these effects are small compared to the difference in the strengths of injected models in our study and those of Jindal et al. (2020), and we thus do not consider this to be the dominating factor in our ability to recover an injected model. Instead, our ability to recover an injected model appears to be limited by the overall noise level of the data, as demonstrated by the white noise test described in Appendix D.1. While SYSREM does not appear to have adequately removed contributions from the Earth’s atmosphere, it has also begun to remove the signal contributed by some injected models. Again, we believe that future analyses of data in the wavelength ranges covered by CARMENES and SPIRou would benefit from exploring alternate methods of removing stellar and telluric lines, including a detailed comparison between the capabilities of SYSREM and Molecfit.

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![Figure 34](image-url) Results of varying the number of iterations of SYSREM used on a data set with a carbon dioxide model injected, as described in Appendix D.3. The model used had a VMR of 10% and a mean molecular weight of 2 amu. The panels are as described in the caption of Figure 33. After six iterations of SYSREM, the model is more readily detected.
