High-resolution Spectroscopic Detection of TiO and a Stratosphere in the Day-side of WASP-33b

Stevanus K. Nugroho1,2,10, Hajime Kawahara2,3, Kento Masuda4,9, Teruyuki Hirano5, Takayuki Kotani6,7, and Akito Tajitsu8

1 Astronomical Institute, Tohoku University, Sendai 980-8578, Japan; sknugroho@astr.tohoku.ac.jp
2 Department of Earth and Planetary Science, The University of Tokyo, Tokyo 113-0033, Japan
3 Research Center for the Early Universe, School of Science, The University of Tokyo, Tokyo 113-0033, Japan
4 Department of Astrophysical Sciences, Princeton University, Princeton, NJ 08544, USA
5 Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Tokyo 152-8551, Japan
6 National Astronomical Observatory of Japan, 181-8588, Japan
7 Astrobiology Center, National Institutes of Natural Sciences, Tokyo, Japan
8 Subaru Telescope, 650 N. Aohoku Place, Hilo, HI 96720, USA

Received 2017 October 10; revised 2017 October 13; accepted 2017 October 14; published 2017 November 14

Abstract

We report high-resolution spectroscopic detection of TiO molecular signature in the day-side spectra of WASP-33b, the second hottest known hot Jupiter. We used the High Dispersion Spectrograph (HDS; $R \sim 165,000$) on the Subaru telescope in the wavelength range of 0.62–0.88 $\mu$m to obtain the day-side spectra of WASP-33b. We suppress and correct the systematic effects of the instrument and the telluric and stellar lines using the SYMREM algorithm after the selection of good orders based on Barnard’s star and other M-type stars. We detect a 4.8 $\sigma$ signal at an orbital velocity of $K_\star = +237.5^{+13.0}_{-9.0}$ km s$^{-1}$ and systemic velocity of $V_\text{sys} = -1.5^{+0.5}_{-0.3}$ km s$^{-1}$, which agree with the derived values from a previous analysis of the primary transit. Our detection with the temperature inversion model implies the existence of a stratosphere in its atmosphere; however, we were unable to constrain the volume mixing ratio of the detected TiO. We also measure the stellar radial velocity and use it to obtain a more stringent constraint on the orbital velocity, $K_\star = 239.0^{+2.0}_{-1.0}$ km s$^{-1}$. Our results demonstrate that high-dispersion spectroscopy is a powerful tool to characterize the atmosphere of an exoplanet, even in the optical wavelength range, and shows a promising potential in using and developing similar techniques with high-dispersion spectrograph on current 10 m class and future extremely large telescopes.

Key words: planets and satellites: atmospheres – planets and satellites: composition – planets and satellites: individual (WASP-33b) – techniques: spectroscopic

1. Introduction

Thermal inversion is still a problem that is not completely understood in the theory of exoplanetary atmospheres. This inversion layer, which is caused by high-temperature absorber molecules, such as TiO or VO, that absorb UV and visible radiation from incoming stellar radiation and heat up the upper atmosphere, was predicted by Hubeny et al. (2003) and Fortney et al. (2008) in a highly irradiated planet. By measuring shallower eclipse depths at 4.5 $\mu$m and 5.6 $\mu$m, caused mainly by $H_2O$ and CO, than at the thermal continuum at the nearby band (3.6 and 9 $\mu$m) using the Spitzer Space Telescope (Spitzer), the first evidence of an inversion layer was reported by Knutson et al. (2008) in the atmosphere of HD 209458b. Although there have been similar observations of a secondary eclipse depth with the same telescope, suggesting the detection of an inversion layer, it was shown by Hansen et al. (2014) that several previous single-transit observations using Spitzer have uncertainties significantly higher than those previously known, which made the measured emission-like features doubtful. Using the CRyogenic high-resolution InfraRed Echelle SPectrograph (CRIRES; Kaeufl et al. 2004) on the Very Large Telescope (VLT), Schwarz et al. (2015) observed the day-side of HD 209458b and reported the nondetection of CO at 2.3 $\mu$m and constrained the nonexistence of the inversion layer to the pressure range of $10^{-1}$–$10^{-3}$ bar, which is consistent with the results of Zellem et al. (2014) and Diamond-Lowe et al. (2014). Despite the nondetection of CO in the day-side of HD 209458b, Snellen et al. (2010) detected a CO absorption feature at 5.6 $\sigma$ using a similar instrument in the transmission spectrum. One of the possible causes of the nondetection is that the average day-side atmosphere of HD 209458b is near isothermal in the pressure range that they probe, which makes the day-side spectrum almost featureless (Schwarz et al. 2015).

Evans et al. (2017) reported the detection of $H_2O$ emission features in a super-hot Jupiter, WASP-121b ($T_\text{eq} \sim 2500$ K), using the combination of the Hubble Space Telescope (HST) and Spitzer. The presence of water was resolved and detected at the 5 $\sigma$ confidence level, strengthening the previous conclusion by Evans et al. (2016), which made WASP-121b the first exoplanet with resolved emission features and a detected stratosphere layer. Their findings also include the possible detection of VO in its atmosphere at the level of $1000 \times$ solar abundance and a thermal inversion-like atmospheric structure, even though they only used a 1D atmospheric model structure and did not take the non-equilibrium chemistry into account. Sedaghati et al. (2017) observed WASP-19b during transit using a low-dispersion spectrograph, FORS2, on VLT. They confirmed the presence of water (7.9 $\sigma$) and simultaneously revealed the presence of TiO (7.7 $\sigma$), strongly scattering haze (7.4 $\sigma$), and sodium (3.4 $\sigma$). They also constrained the relative abundance of those molecules; however, the presence of a thermal inversion remains unproved because a transmission
Table 1
System Parameters of WASP-33

| Parameter                      | Value                           |
|--------------------------------|---------------------------------|
| WASP-33                        |                                 |
| $M_\star$ ($M_\odot$)          | $1.561^{+0.045}_{-0.079}$       |
| $P$ (days)                     | $1.512 \pm 0.04^b$              |
| $R_\star$ ($R_\odot$)          | $1.495^{+0.031}_{-0.021}$       |
| $L_\star$ ($L_\odot$)          | $1.509^{+0.014}_{-0.027}$       |
| Spectral Type                  | A5                              |
| $T_{\text{eff}}$ (K)            | $7400 \pm 200^c$                |
| log $g$                        | $4.3 \pm 0.2$                   |
| [Fe/H]                         | $0.1 \pm 0.2^c$                 |
| [M/H]                          | $0.1 \pm 0.2^c$                 |
| Center-of-mass velocity (km s$^{-1}$) | $-2.19 \pm 0.09^c$             |
| $v_{\text{rot}} \sin i_*$ (km s$^{-1}$) | $86.63^{+12}_{-13}$           |
| $d$ (pc)                       | $117 \pm 2$                     |
| WASP-33b                       |                                 |
| $T_{\text{eq}}$ (2450000 (BJD)) | $6934.77146 \pm 0.00059^d$      |
| $P$ (days)                     | $1.2197^{+0.014}_{-0.029}$      |
| $T_{\text{ingress}}$ (days)    | $0.0124 \pm 0.0002^c$          |
| $T_{\text{transit}}$ (days)    | $0.1143 \pm 0.0002^c$          |
| $a/R_*$                        | $3.69 \pm 0.01^a$               |
| $i$ (°)                        | $88.69^{+0.031d}_{-0.020}$      |
| 2015 $M_\star$ ($M_\odot$)     | $3.266 \pm 0.726^a$            |
| $R_\star$ ($R_\odot$)          | $1.679^{+0.019a}_{-0.030}$      |
| log $R_\star$ [CGS]            | $3.46^{+0.04}_{-0.12}$         |
| $K_\star$ (km s$^{-1}$)        | $231.11^{+2.20a}_{-2.97}$       |
| $228.67^{+0.00}_{-0.04}$        | $227.81^{+1.56}_{-1.59}$        |

Notes.

$^a$ Adopted from Kovács et al. (2013).
$^b$ Adopted from Smith et al. (2011).
$^c$ Adopted from Collier Cameron et al. (2010).
$^d$ Adopted from Johnson et al. (2015).

The nondetection of TiO or VO can be caused by several factors. Hubeny et al. (2003) and Spiegel et al. (2009) suggested that gravitational settling could drag TiO/VO from the upper atmosphere to the colder layers in the deeper atmosphere. Meanwhile, owing to high-speed winds of the tidally locked hot Jupiter, condensed molecules can also be brought into the colder night-side of the planet. If the temperature of the atmosphere is below the TiO/VO condensation level, it can condensate, and if the vertical mixing rate, which is related to the temperature of the planet atmosphere, is not high enough, it cannot be redistributed to the upper atmosphere. This effect is called the cold-trap effect. Knutson et al. (2010) found a possible connection between the UV chromospheric stellar activity and the existence of an inversion layer in the atmosphere of known hot Jupiters. Hot Jupiters orbiting active stars tend to have no inversion layer, and those orbiting quiet stars show evidence of the existence of an inversion layer in their atmosphere. Knutson et al. (2010) suggested that the increased UV intensity can probably destroy the compounds that are responsible for creating an inversion layer. Meanwhile, using high-dispersion spectroscopy, Hoeijmakers et al. (2015) reported the inaccuracy of the TiO line list that was used at wavelengths shorter than 6300 Å. The accuracy level, however, tends to increase at longer wavelengths, which was shown by the cross-correlation result between the spectrum of Barnard’s Star and the model spectrum created using the corresponding TiO line list (see Figure 9 of Hoeijmakers et al. 2015).

Recently, the direct detection of molecular signature in exoplanet atmospheres using high-dispersion spectroscopy has become one of the most widespread approaches in attempts to characterize exoplanets (e.g. Snellen et al. 2010; Crossfield et al. 2011; Birkby et al. 2013; de Kok et al. 2013; Hoeijmakers et al. 2015; Schwarz et al. 2015; Birkby et al. 2017; Esteves et al. 2017). Unlike low-dispersion spectroscopy, high-dispersion spectroscopy can resolve molecular bands into individual absorption lines. The variation of Doppler shifts, which is caused by orbital movement, during observations enables absorption lines in the exoplanet spectrum to be distinguished from telluric lines and ensures the unambiguous detection of specific molecules. Owing to these resolved individual lines, it is also possible to investigate several physical parameters of the exoplanet such as the axial tilt (Kawahara 2012), projected equatorial rotational velocity (Snellen et al. 2014), wind speed (Brogi et al. 2016), and the thermal inversion layer (Schwarz et al. 2015) of the planet. Obtaining the exoplanet spectrum can be done by cross-correlating the data with the exoplanet atmosphere spectrum model after removing telluric and stellar lines using a specific method.

We observed WASP-33b (Smith et al. 2011), which is the second hottest known hot Jupiter (wavelength-dependent
brightness temperature of 3620 K), orbiting quiet δ Scuti stars. It has a retrograde orbit with a period of ~1.22 days. It is an ideal choice for transmission spectroscopy measurements owing to its unusually large radius (Collier Cameron et al. 2010) and its high temperature, making it not only suitable for secondary eclipse spectroscopy measurements, but also as the main target to find TiO/VO in its atmosphere, as the cold-trap effect is unlikely at this temperature level.

In this paper, we report the direct detection of TiO molecules and a stratosphere layer in WASP-33b, based on ground-based observations of the day-side emission spectrum in the visible wavelength range (6170–8817 Å). The observation, data reduction, and systematic effect removal (including the correction of the blaze function variation, common wavelength grid, and telluric and stellar line removal) are described in Section 2. We also examine our methods to create the model spectrum and to cross-correlate the data with the model spectrum. Here, we also explain the method for confirming the radial velocity of WASP-33 and the accuracy of the TiO line list we used. In Section 3, the possibility of a signal detection of TiO and the order-by-order (order-based) optimization of the SYSREM algorithm is explored. Here, we also show the final result after the optimization and the statistical test. This is followed by a discussion and the conclusions of our findings in Section 4.

2. Observation and Data Reduction

2.1. Subaru Observation of WASP-33

We observed WASP-33 on UT 2015 October 26 (see Table 1 for stellar and exoplanet physical and dynamical parameters) using the High Dispersion Spectrograph (HDS; Noguchi et al. 2002) at the f/12.71 optical Nasmyth focus of the Subaru 8.2 m telescope (proposal ID: S15B-090, PI: H. Kawahara). The observation was conducted in a standard NIRc set up (without an iodine cell) with Messia5, 2×1 binning setting, and without an image rotator. Image slicer 3 (Tajitsu et al. 2012), with slit width = 0.2, was used, resulting in the highest spectral resolution of \( R = 165,000 \) (1.8 km s\(^{-1}\) resolution); the data were sampled by two detectors (blue and red CCDs) with 4100 × 2048 pixels (0.9 km s\(^{-1}\) per pixel), containing 18 orders covering 6170–7402 Å and 12 orders covering 7537–8817 Å. We obtained 52 spectra of WASP-33, each with an exposure time of 600 s, from air mass 2.97–1.96 on the other meridian covering 0.23–0.56 exoplanet orbital phases (see Table 1 for the ephemeris and the derived orbital period; the orbital coverage of our observation is shown by the thick red line in Figure 1) with a typical seeing of ~0″6–0″7.

2.2. M-dwarf Spectra

Hoeijmakers et al. (2015) showed that the TiO line list they used is not accurate at short wavelengths (<6000 Å); however, it tends to be more accurate at longer wavelengths. For robustness of the analysis, we checked the accuracy of the TiO line list we use in this paper, comparing it with the spectra of Barnard’s Star (M4V) and HD 95735 (M1.5V), as TiO is commonly found in the atmosphere of M-type stars and brown dwarfs (Burrows & Sharp 1999; Burrows et al. 2001). In 2016, we observed Gl 752A (M3V) and HD 173739 (M3V) with the Subaru telescope using the same instrumental configuration as in 2015 (proposal ID: S16A-107, PI: H. Kawahara). To check the robustness of our cross-correlation, we also downloaded and used the calibrated spectrum of Proxima Centauri from the ESO Science Archive Facility. The spectrum was obtained by XSHOOTER at VLT between 5336.6 Å and 10200 Å with a resolution of \( R = 18,000 \) (proposal ID: 092.D-0300(A), PI: Neves).

2.3. Standard Reduction

The data were reduced using IRAF tools\(^\text{11}\) and a custom-built application written in Python 2.7. We corrected the overscan and nonlinearity using CL scripts obtainable from the HDS Web site\(^\text{12}\) before debiasing the frames. During the analysis of Narita et al.’s (2005) data, Snellen et al. (2008) noticed the nonlinearity effect in HDS. After fixing this problem empirically, the analysis turned up the detection of sodium in the atmosphere of HD 209458b. The CCD response

---

\(^{11}\) The Image Reduction and Analysis Facility (IRAF) is distributed by the US National Optical Astronomy Observatories, operated by the Association of Universities for Research in Astronomy, Inc., under a cooperative agreement with the National Science Foundation.

\(^{12}\) http://www.subarutelescope.org/Observing/Instruments/HDS/index.html
(gain) for high signal-to-noise (S/N) spectra is higher than those in a lower S/N spectra, which would make the correction of telluric and stellar lines difficult. This problem was solved by Tajitsu et al. (2010), who provided a CL script to correct this effect after applying the overscan correction. The scattered light in the interorder area was fitted individually with a cubic spline function along the slit and dispersion direction using `apscat`ter for the arc lamp frame, and smoothed and subtracted from all science frames. A median flat frame was calculated from 71 dome-flat frames to correct the pixel-to-pixel sensitivity variation and normalized using the `apnormal`ize task in IRAF in order to conserve the fringe pattern along the slit direction.

**Table 2**
Models of Planetary Atmosphere

| Name  | T/P Profile                | log VMR |
|-------|----------------------------|---------|
| FI    | Full inversion             | −7      |
| NI    | No inversion               | −7      |
| H     | Realistic inversion (Haynes et al. 2015) | −4 to −10 |

**Figure 3.** Reduction process for each order of both blue (a) and red CCDs (b). The first row [1] shows an example of the normalized 1D spectrum of WASP-33 following the correction of the blaze function variation and the common wavelength grid iteration. The next row [2] shows the 2D spectrum with the wavelength as the horizontal axis, each label representing the median wavelength of the order, while the vertical axis is the frame number. The third row [3] shows the final reduced spectra after the correction of the blaze function in the common wavelength grid. The variation of brightness along the frames for all orders is due to the blaze function variation. The fourth row [4] shows the mean subtracted spectra as the input to SYSREM. The fifth [5] and sixth [6] rows show the residual spectra after running SYSREM with one and four iterations and through the double high-pass filter; at the latter stage almost all telluric lines have been removed. The masked bad regions are shown by gray areas in all rows except the first one.
order tracer of each order for the blue and red CCDs, respectively; divided them by the slice of the normalized median flat frame; and sum combined. If a larger width were used, a high-frequency noise would appear along the wavelength in the extracted spectra, which is caused by the edge of the aperture defined earlier in apnormalize using a median flat frame. We derived the wavelength solution by identifying 133 emission lines of thorium–argon arc lamp frames taken at the beginning and the end of the observation, and fitted with a fifth- and third-order Chebyshev function corresponding to the dispersion and slit directions, respectively, using ecidentify. The pixel rms value of the residual fitting was ~0.0012 for both CCDs. Then, the spectra were assigned by interpolating between the preceding and the following thorium–argon arc lamp frames with respect to the observation time, using refspecl with the relative distance of the spectra to the reference spectra as the weight of the interpolation. Then, the wavelength solution was applied using dispcor. These steps were applied to the non-normalized median flat frame to create the corrector for the blaze function. All science frames were then divided by the blaze function corrector to create the final reduced frames. Then, the next step is to correct the variation of the blaze function along the time; this is given in detail in Appendix A.

2.4. Common Wavelength Grid

We measured the shifts of the spectrum during the observation by measuring the shifts of the strong telluric lines relative to the reference spectrum. First, we detected telluric lines using peakutils14 (15–20 lines on average per selected order) in the order that contains well spread-out telluric lines in the wavelength direction. We then fitted each line with a Gaussian function to determine the precise centroid of each line and compared it with the centroid of the same lines in the first frame. The relative shift of each order was calculated by taking the median combination of the shifts in that order. There are order-dependent shifts of about 0.05 pixels, but because the information for the order that does not have strong telluric lines is not available and the value is too small to affect the result (0.05 pixels corresponding to ~0.04 km s$^{-1}$), we decided to ignore it. The results of all selected orders were combined to estimate the shift of the corresponding frame by calculating its weighted median combined.

The amplitude of the relative shifts is about 0.13 and 0.08 pixels (~0.12 and 0.07 km s$^{-1}$) for the blue and red CCDs, respectively. Noticeably, the general trend of the shifts is correlated with the shifts of the temperature inside the dome ($\Delta T \sim 1.75$ K) during the observation (see Figures 2(a) and (b)). This wavelength–temperature-shift relation trend is relatively weaker than those for CRIRES in VLT reported by Brogi et al. (2013; 1.5 K changes in the temperature, corresponding to 1.5 pixel shifts), who gave a nondetection of the 51 Peg b signal due to the odd–even effect for detector 4. Then, the spectra were shifted with spline interpolation, based on the weighted median-combined shift of each frame, and then re-sampled into a common wavelength bin. The spectra of each order were then stacked in a matrix with wavelength bin values in its columns and spectrum numbers (or time/orbital phases) in its rows. For each wavelength bin, 5σ clipping was performed to identify any bad pixels/cosmic rays, which are replaced by the mean value of the bin. We excluded these bad regions, which are 5.30% and 7.19% of all pixels in blue and red CCDs, respectively, from the rest of the analysis, mostly because they are on the edge of the CCD.

2.5. Removal of Telluric and Stellar Absorption Lines

In the studied wavelength range, telluric and stellar absorption lines dominate the spectrum, while the exoplanet to stellar flux contrast is expected at the level of $10^{-3}$ (when extrapolated from the best-fit spectrum in Haynes et al. 2015). The removal of telluric and stellar lines is critical in order to detect the TiO

---

14 https://bitbucket.org/lucashnegri
signature by cross-correlation, as the exoplanet spectrum is buried under sharp noises due to those lines. The spectrum of WASP-33b is expected to be Doppler-shifted from $+230 \text{ km s}^{-1}$ (at its maximum) to $-54 \text{ km s}^{-1}$ (at the end of the observation), while the telluric and stellar lines remain relatively stationary during the course of the observation. Telluric lines, which are dominated mostly by water and oxygen lines, vary in strength due to the changes in geometric air mass and water vapor column of the atmosphere.

The quasi-static telluric and stellar absorption lines were removed by implementing the SYSREM algorithm to remove systematic effects (variation of atmospheric condition, changing of CCD efficiency, variation of point-spread function, etc.) without any priors in a large set of light curves (Tamuz et al. 2005; Mazeh et al. 2007). It was used either in the detrending/systematic effects removal of transit surveys (e.g. SuperWASP, CoRoT light curves; Collier Cameron et al. 2006; Ofir et al. 2010) or in the removal of quasi-static telluric lines in a similar analysis to this work (e.g., Birkby et al. 2013, 2017; Esteves et al. 2017). Each wavelength bin (4100 wavelength bins per order on average) is treated as a “light curve” consisting of 52 frames (including the frames when WASP-33b is in the secondary eclipse phase). Then, each “light curve” was subtracted from their mean value before applying the SYSREM algorithm order by order (fourth row in Figure 3). The detailed description of the SYSREM algorithm is given in Appendix B.

The step-by-step removal of telluric lines can be seen in Figure 3. It can be noticed that there are curve-shaped features that can be seen in the blue CCD spectra matrix, and the degree of curvature decreases with increasing wavelength. These features can be caused by the imperfection of the correction of the blaze function variation. As the residual was cross-correlated with the high-frequency TiO features, this feature does not affect the results, and these were roughly removed after a double high-pass filter was applied (see Figure 3).

Any linear systematic variation along all wavelength bins in each order can be found and removed from the spectrum starting with the most significant one, such as air mass variation. Ideally, the expected residual is the Doppler-shifted exoplanet spectrum only, with additional noise. We perform two cases of SYSREM reduction. In the first, we remove the first 10 systematics (henceforth SYSREM iteration, $N_{\text{sys}} = 10$) for all of the orders (SYSREM with common iteration number in Section 3.1). This simple procedure gives a conservative estimate of the signal detection. The second attempt is to determine the optimum number of subsequent SYSREM iterations for each order that gives the optimum systematic removal (Order-based SYSREM optimization in Section 3.2). The latter is based on the fact that SYSREM tends to remove the exoplanet spectrum after the Doppler-shifted variation dominates the systematic change in the spectrum.

Before performing cross-correlation for each residual, we applied a double high-pass filter similarly to the case for the M-dwarf star spectrum. We used a smoothing function with a 25 pixel width for the first filter and a 51 pixel width for the second filter to remove any low-frequency variations along the spectrum, and then cross-correlated with a grid of the Doppler-shifted WASP-33b model spectrum. Then, the values of each wavelength bin were weighted by their noise, which is defined by the standard deviation of the bin as a function of time. The

Figure 5. WASP-33b spectrum model using the $T/P$ profile of Haynes et al. (2015). The left panel shows the WASP-33b model spectrum with various VMRs. The vertical axis shows the planet to star flux contrast in the level of $10^{-3}$. The right panel shows our adopted temperature profile for the WASP-33b atmosphere.
results of this removal process are 10 sets of smoothed weighted SYSREM residuals for each CCD.

2.6. Spectral Template

To constrain the existence of TiO molecules in WASP-33b emission spectra by cross-correlation, model spectra were generated with various profiles and volume mixing ratios (VMRs) of TiO, assuming several atmospheric models as described in Table 2. Three different temperature–pressure (T/P) profiles were adopted, which described the average vertical temperature structure of the planetary day-side atmosphere: full inversion (FI), non-inversion (NI) as shown in the right panels of Figure 4, and T/P profile from Haynes et al. (2015), known as the H-model, as shown in the right panel of Figure 5. For the NI model, it was assumed that the temperature decreases with a constant lapse rate from $P_0 = 10^7$ bar with $T_0 = 3700$ K to $P_1 = 10^{-3}$ bar with $T_1 = 2700$ K. For the FI model, the temperature increases from $P_0 = 10^7$ with $T_0 = 2700$ K to $P_1 = 10^{-3}$ with $T_1 = 3700$ K. For both models, we assumed a constant TiO concentration at solar abundance level, that is, $\text{VMR} = 10^{-7.2}$, and no other molecule in the atmosphere. For the H-model, seven constant VMRs of TiO from subsolar to supersolar abundance level were assumed, $\text{log VMR}_{\text{TiO}} = [-4, -5, -6, -7, -8, -9, -10]$. The atmosphere was divided into 50 layers, which were evenly spaced in log pressure between $10^2$ to $10^{-3}$ bar, and the altitudes were calculated by assuming a hydrostatic H2-dominant atmosphere and using the derived mass and a radius of WASP-33b from the reference (Table 1). We also modeled the non-inverted atmosphere (henceforth the M-dwarf model) with $T_0 = 2600$ K at $P_0 = 0.01$ bar and $T_1 = 4000$ K at $P_1 = 1$ bar, assuming a constant rate of temperature change with log pressure, resulting in TiO absorption features only for $\text{log VMR} = -7$.

The cross-section of the molecules was calculated using “Python scripts for Computational Atmospheric Spectroscopy” (Py4CATS15). The procedure for computing the cross-section is described in Appendix C. Then, the cross-sections were combined into continuum absorption coefficients and integrated along the line of sight through the atmosphere, resulting in delta optical depths per layer. The Schwarzschild equation was solved by integrating the Planck function versus the monochromatic transmission along the line of sight and convolved with a Gaussian kernel to match with the HDS resolution. In total, we produced nine WASP-33b mock spectra and one non-inverted model for TiO line list accuracy analysis: one full inversion (FI-spec), one no inversion (NI-spec), seven spectra for Haynes (H-spec), and one M-dwarf model. See Figure 4 for FI-spec and NI-spec, Figure 5 for H-spec, and Figure 6 for five M-dwarf spectra plus one M-dwarf model spectrum.

In this analysis, the systemic velocity ($V_{\text{sys}}$) is one of the important parameters to confirm the detection (if there is any); thus, by measuring the radial velocity (RV) of WASP-33 and comparing it with the previous results, the confidence and robustness of our analysis are improved. Instead of creating the WASP-33 comparison spectra by ourselves, we used the stellar model spectrum from Coelho (2014) for $T_{\text{eff}} = 7500$ K, log $g = 4.5$, $[\text{Fe/H}] = +0.2$, and $[\alpha/\text{Fe}] = 0$. The stellar model spectrum was convolved to the HDS resolution and rotationally broadened to resemble the Doppler broadening caused by its fast rotation (henceforth the Coelho model spectrum).

2.7. System Velocity from Stellar Spectra

To measure the RV of the WASP-33 system, we analyzed the standard reduced WASP-33 spectra and masked the telluric lines of the selected order that contains significant stellar absorption lines. Then, the spectra were cross-correlated order by order with the Doppler-shifted Coelho model spectrum from $-100$ km $s^{-1}$ to $+100$ km $s^{-1}$ with 0.1 km $s^{-1}$ intervals. In this cross-correlation, only the spectra in the blue CCD was used because there are a lot of telluric lines and fewer stellar absorption lines in the red CCD spectrum. For each selected order, the RV value with the highest cross-correlation signal was extracted and median-combined to calculate the RV of WASP-33 for the corresponding frame. Then, the weighted

---

15 See http://www.libradtran.org for details.
The median-combined RV of all frames was calculated, following the correction of the barycentric RV difference to obtain the final WASP-33 RV value.

The results can be seen in Figure 7(b), and the median of the measured RV is $-3.02 \pm 0.42$ km s$^{-1}$. Although this value is different from the value of $-9.2 \pm 2.8$ km s$^{-1}$ (Gontcharov 2006).
in the SIMBAD database, our result is consistent with that of Collier Cameron et al. (2010), which used the Doppler tomography technique to confirm the existence of the planet and measured the center-of-mass velocity (see Table 1). Therefore, we used this value as the RV of the WASP-33 system, which is taken into consideration when evaluating the result of the WASP-33b versus TiO model cross-correlation analysis.

2.7.1. Line List Accuracy and Excluding Bad Orders

To check the TiO line list accuracy, five standard reduced M-dwarf spectra were cross-correlated order by order with the M-dwarf model. The model spectra were Doppler-shifted from −80 km s⁻¹ to +80 km s⁻¹ relative to the RV of the expected target from the SIMBAD database with 1 km s⁻¹ intervals. The object and model spectrum was divided by their continuum...
profile, calculated by applying a double high-pass filter with 501 pixels and 1001 pixels of smoothing function before cross-correlation, in order to maintain the cross-correlation scale (from −1 to 1).

The cross-correlation results for five M-dwarf spectra versus the M-dwarf model are shown in Figure 8. As Hoeijmakers et al. (2015) expected, the accuracy of the TiO line list improved in the longer wavelength, although there are cross-correlation functions (CCFs) of several orders, which are blueshifted from their expected RV, and several others do not have any significant peak. For the other orders, the peaks are located at their expected RVs. The shifts are most likely caused by the inaccuracy of the TiO line list itself, because the first three orders of the blue CCD show similar blueshifted CCFs for the five different M-dwarf spectra. The shift is about ∼21 km s$^{-1}$ (shown by the blue dashed line in Figure 8). There are several orders that have no significant peak, which can be caused by the imperfection of our simple atmosphere modeling or the inaccuracy of the line list. Note that all orders that have no significant CCF peak have a large bad region, except the last order of the red CCD (see Figure 3 and/or Figure 8). These bad orders are excluded from the rest of the analysis, including order 2 in the red CCD due to heavy contamination by strong telluric lines.

3. TiO Signal Detection

3.1. Results from SYSREM with a Common Iteration Number

As described in Section 2.5, we first analyze the spectra with a common SYSREM iteration number for all orders. A grid of the Doppler-shifted WASP-33b model spectrum was cross-correlated with weighted SYSREM residuals. The Doppler-shifted model spectrum covers the planet RV ($RV_p$) between $-169.69$ km s$^{-1}$ ≤ $RV_p$ ≤ $+393.30$ km s$^{-1}$ with 0.5 km s$^{-1}$ intervals, corresponding to half of the HDS sampling resolution. For each detector, the CCFs of every good order (all orders excluding the bad orders explained in Section 2.7.1) were summed. This value is listed in the CCF matrix with a dimension of 1127 (RV as column) × 52 (orbital phase as row). Then, the CCF matrix of the blue and red CCDs was summed to calculate the final CCF matrix. These steps were done for all SYSREM residuals.

We then calculate the CCF map in the $K_p$–$V_{sys}$ plane for all spectrum models by performing the following steps. The CCF of the frames (40 frames in total, excluding the frames when WASP-33b was expected to be in the secondary eclipse phase) was integrated along the expected RV$_p$ curve,

$$RV_p(t) = K_p \sin(2\pi\phi(t)) + V_{sys} + \nu_{bary}(t),$$

with

$$\phi(t) = \frac{t - T_0}{P},$$

where $\nu_{bary}(t)$ is the barycentric correction, $\phi(t)$ is the planet orbital phase, $t$ is the mid-observation time in BJD, $T_0$ is the ephemeris, $P$ is the orbital period of the planet, $K_p$ is the semi-amplitude of the RV of the planet, and $V_{sys}$ is the systemic velocity. We consider the RV of the planet semi-amplitude to be between $+150$ km s$^{-1}$ ≤ $K_p$ ≤ $+310$ km s$^{-1}$ and the systemic velocity to be between $-80$ km s$^{-1}$ ≤ $V_{sys}$ ≤ $+80$ km s$^{-1}$ with 0.5 km s$^{-1}$ steps. The result is a 321 ($V_{sys}$ as column) × 320 ($K_p$ as row) CCF matrix. Then, this matrix was divided by its standard deviation to make the $K_p$–$V_{sys}$ S/N map.

Figure 9 shows the $K_p$–$V_{sys}$ S/N map for $N_{sys} = 4$ (H-spec) and $N_{sys} = 10$ (H-, FI-, and NI-spec models). In all of the cases except for NI-spec, we detected positive peaks with >4$\sigma$, while the map for NI-spec exhibits a negative peak at the same place. The maps for H-spec and FI-spec exhibit a strong peak in almost all SYSREM iteration numbers at $K_p = +237.0$ km s$^{-1}$ and $V_{sys} = -1.5$ km s$^{-1}$ (henceforth peak A). Among all H-spec, the strongest signal was found in log VMR = −8. This peak is also the strongest one in the $K_p$–$V_{sys}$ S/N maps of both FI-spec and NI-spec for most of the SYSREM iteration numbers, although for NI-spec the value is negative. The positive value of peak A in H-spec and FI-spec, and the negative value in NI-spec suggested that a non-inversion atmosphere is unlikely for WASP-33b if peak A is the real signal. The second strongest peak was detected at $K_p = +192.0$ km s$^{-1}$ and $V_{sys} = +19.5$ km s$^{-1}$ (henceforth peak B) in SYSREM iteration number = 2 only.

Figure 10 shows the S/N of peaks A and B as a function of the SYSREM iteration, although peak B is unlikely to be a real signal, due to its physically non-realistic $K_p$ and $V_{sys}$ values compared with the expected value from previous studies; it was chosen as a representative of the noise/false-positive signal. The S/N of peak B decreases as the SYSREM iteration number increases. The S/N of peak A increases from SYSREM iteration = 1 until SYSREM iteration = 4 and then decreases until SYSREM iteration = 6 before beginning to increase again until SYSREM iteration = 10. The increase of the S/N of peak A after SYSREM iteration = 6 is most likely due to the difference level in the telluric and/or stellar line removal in each order. It can be seen in Figure 9(a) for SYSREM iteration = 4, where multiple (five) peaks within the 1$\sigma$ level from the strongest peak can be found (white color). On the other hand, in Figure 9(b), there are only two peaks, peak A and another one at about $K_p \sim +160.0$ km s$^{-1}$ and $V_{sys} \sim -20$ km s$^{-1}$. From the curve of Figure 10, it is natural to adopt $N_{sys} = 10$ as the fiducial iteration number. Because the

16 The nodal precession of WASP-33b caused the orbital inclination to evolve from ∼86°/61 in 2008 to 88°/70 in 2014 (Johnson et al. 2015), and based on the Smith et al. (2011) analysis of its orbital eccentricity, we can safely assume a circular orbit with orbital inclination ∼90° to calculate RV$_p$.  

---

Figure 10. S/N of peaks A and B along the SYSREM iteration number, $N_{sys}$, for H-spec (log VMR = −8). The blue diamond line is the S/N of peak A and the red circle dotted line is the S/N of peak B.
The level of systematics (telluric lines) should be different for each order, and thus to find the optimized SYSREM iteration number of each order, the following steps were also performed. A scaled artificial signal was injected at the detected RV ($K_p = +237$ km s$^{-1}$ and $V_{sys} = -1.5$ km s$^{-1}$) in the spectra before telluric and stellar line removal. The scaling was performed according to the equation

$$F_{\text{scaled pm}}(\lambda) = sc \times F_{\text{pm}}(\lambda) \left( \frac{R_p}{R_{\text{star}}} \right)^2,$$

(3)

where $sc$ is the scaling constant, $F_{\text{scaled pm}}$ is the scaled artificial signal, $F_{\text{pm}}(\lambda)$ is the planet model spectrum (H-spec with log VMR = −8) from the integration of the Planck function versus the monochromatic transmission along the line of sight (see Section 2.6), $F_{\text{star}}(\lambda)$ is the blackbody flux of $T = 7400$ K representing the continuum level of the WASP-33 flux, and $R_p$ and $R_{\text{star}}$ are the planet and star radii, respectively.

To check the dependence on the strength of the injected signal, we adopt five different injected signals with $sc = [0.2, 0.4, 0.6, 0.8, 1.0]$. The injected signals are broadened by a rotation kernel, using fastRotBroad from PyAstronomy with $\nu\sin{i} = 0.4$ times the expected projected velocity of WASP-33b (calculated by assuming a tidally locked condition with the parameter in the Table 1 referring to the typical broadening width of a tidally locked exoplanet as shown in Kawahara 2012). We convolve these with a box function to

Figure 11. $S_{\text{max}}/n$ of all orders for various SYSREM iteration numbers. The vertical lines mark the SYSREM iteration number that made the signal strength optimum. The blue circle, yellow asterisk, green diamond, red square, and purple cross are the $S_{\text{max}}/n$ of the recovered injected signal with $sc = [0.2, 0.4, 0.6, 0.8, 1.0]$, respectively. The number in the white box at the bottom left of each panel represents the order number and the color represents the CCD (blue or red).

Figure 12. Standard deviation of the spectrum of each order with their corresponding optimized SYSREM iteration number. The blue cross and the red circle indicate the spectrum in the blue and red CCDs, respectively. The value of the standard deviation represents the amount of telluric and/or stellar line contamination for every order.
The CCF of each order of each frame was aligned to the planet rest frame according to the injected signal itself. Then, the aligned CCFs of all frames, except the frames corresponding to the secondary eclipse, were summed to create the total mean CCF. To examine the exoplanet signal for various combinations of optimum SYSREM iteration numbers, we were able to choose the optimum SYSREM iteration numbers. For the blue and red CCDs, the optimum SYSREM iteration numbers are [2, 2, 3, 3, 2, 2, 2, 3, 2, 8, 2, 1, 5, 3, 1, 3, 5, 2, 7, 2, 8, 2, 2, 2] and [2, 3, 5, 2, 3, 4, 2, 8, 3, 9, 3, 5], respectively, for each of their orders. Figure 12 shows the level of telluric and/or stellar line contamination of each order, which is represented by the standard deviation value of the standard reduced spectrum in that order and its corresponding optimum SYSREM iteration number. One can see the tendency of the optimum SYSREM iteration number to increase as it exhibits more telluric and/or stellar lines in the spectrum, except for the one in the bottom right of the figure (the order having many O2 lines).

Using the optimum SYSREM iteration number, the mean CCF map was calculated for all of the spectrum models as shown in Figure 13 (left panel). Then, the CCF was aligned to the rest frame of the planet (middle panel). The TiO signal can be seen in the left panels as a positive (dark) signal with an arc shape for H- and Fl-spec and as a negative (bright) one for Ni-spec. In the middle panels of the figures, the planet signal was aligned such that it can be seen as a dark trail in the expected orbital phase while there is no offset when the planet is behind the star. This feature supports the atmospheric origin of the CCF signal. The exposure time for a single frame is 600 s, which corresponds to ~7 km s^{-1} at the near-eclipse phase. This long exposure time should have smeared out the day-side spectrum due to the change in the radial component of the orbital velocity of the planet, especially in the phases near the secondary eclipse. This smearing effect may account for the fact that the signal is only visible at phases \leq 0.35, although it should be stronger at phases \geq 0.35 because a larger part of the day-side of the WASP-33b is visible.
Figure 15. Histogram of the in-trail and out-trail mean CCF distribution; the in-trail distribution is slightly shifted from the out-of-trail distribution.

Figure 16. Q–Q plot of the out-of-trail distribution which shows that the distribution is Gaussian until 4σ.

Figure 17. Significance map after converting from the p-value from Welch’s t-test using the erf function for the most significant detected signal with the H-spec model spectrum of log VMRTiO = −8. The black dashes show the most significant signal, the white dashes show the expected Kp and Vsys, and the color bar grid interval is 1σ, and the white area also represents the 1σ error of the detected signal.

very precise for a transiting exoplanet, our observation provides the first model-independent measurement of the mass of the host star. Using the period of WASP-33b from a previous study (see Table 1), the measured mass of the host star is found to be $M_\star = 1.73^{+0.04}_{-0.02} M_\odot$, which is larger than previously reported values.

3.3. Statistical Tests

The in-trail CCF (henceforth the in-trail signal) was compared with the out-of-trail CCF (henceforth the out-of-trail signal) by performing Welch’s t-test to check if the mean is the same, assuming that two distributions were drawn from the same parent distribution, using the SciPy module in Python 2.7. We used Equation (1) to calculate the expected RVp for the same range as the ones used for the Kp−Vsys CCF maps, and took the 1 pixel mean CCF value at the closest RV to RVp. The out-of-trail signal contains all mean CCF values, except the in-trail signal.

The out-of-trail and in-trail signal histograms (width of the in-trail signal = ±3 pixels) were plotted (see Figure 15). The in-trail signal distribution is shifted further from the out-of-trail signal distribution. The distribution of the in-trail signal is clearly shifted from the zero values. From the Q–Q plot (see Figure 16), it can be seen that the out-of-trail signal distribution is a Gaussian distribution until 4σ; therefore, we can safely convert the half p-value to the σ value of the detection significance using an error function. Welch’s t-test shows that the in-trail distribution deviates from the out-of-trail signal distribution by 5.0σ (see Figure 17), in line with the S/N of this peak detection.

4. Discussion and Conclusions

We confirmed the previously claimed inaccuracy of the TiO line list for wavelengths shorter than 6300 Å (see Hoeijmakers et al. 2015). We also showed that the line list accuracy is high enough for longer wavelengths, which was considered in processing order-based optimization; therefore, our analysis no

17 The output from the scipy module is the two-tailed p-value.
longer suffers from the inaccuracy issue. By measuring the RV of the host star, we also confirmed the measurement of Collier Cameron et al. (2010), which differs by $\sim 4$ km s$^{-1}$ from the SIMBAD database. This confirmation gives us a narrow $v_{\text{sys}}$ search space to find a possible exoplanet signal.

We reported a TiO molecule signature detection in the day-side spectra of WASP-33b at a 4.8$\sigma$ confidence level, which provided direct evidence of the existence of TiO in the atmosphere of the hot Jupiter. The detection levels for VMR = $-8$, $-9$, and $-10$ (H-spec) lie within 1$\sigma$ from the highest one (VMR = $-8$); moreover, in our analysis, we did not use a self-consistent atmospheric model; thus, the constraint on the VMR cannot be obtained directly from our result only. Our TiO molecular detection for H-spec and FI-spec confirmed the existence of a stratosphere (thermal inversion layer) in the day-side of WASP-33b, as has been previously claimed by several studies (e.g., Haynes et al. 2015; von Essen et al. 2015). The full inversion $T/P$ profile has also been reported for another super-hot Jupiter, WASP-121b, by Evans et al. (2017), which resolved the emission spectral feature of H$_2$O at near-infrared wavelengths, using HST. Our result is complementary to the TiO detection using low-dispersion spectroscopy in WASP-19b by Sedaghati et al. (2017), who were able to constrain the relative abundance of TiO (0.12 p.p.b) but could not provide information about the $T/P$ profile as they were only able to measure the transmission level of the molecules in the atmosphere. The constraint on the relative abundance level of TiO in WASP-33b can be obtained by analyzing it using a self-consistent atmospheric model and/or by combining low- and high-dispersion spectroscopy in order to introduce a more precise constraint of the relative abundance of each detected molecule and the $T/P$ profile of the exoplanet atmosphere (Brogi et al. 2017).

By observing for about nine hours only using the 8.2 m Subaru telescope, we were able to detect a significant signature of TiO in the atmosphere of WASP-33b. Our results demonstrate that high-dispersion spectroscopy is a powerful tool to characterize the atmosphere of an exoplanet and shows a promising potential for the development of similar/more advanced techniques for the Infrared Doppler instrument (Kotani et al. 2014) in the Subaru telescope and for extra large telescope facilities in the future, as suggested by several authors (e.g., Kawahara & Hirano 2014; Snellen et al. 2015).

This work was based in part on data collected on the HDS at the Subaru Telescope, which is operated by the National Astronomical Observatory of Japan. We thank our anonymous referee, whose insightful comments improved the manuscript. S.K.N. acknowledges support from the Indonesia Endowment Fund for Education Scholarship. S.K.N. also acknowledges Toru Yamada for fruitful discussions during the analysis of the data. H.K. is supported by a Grant-in-Aid for Young Scientist (B) from the Japan Society for the Promotion of Science (JSPS), No. 17K14246, and the Astrobiology Center from NINS, No. AB291003. T.H. is supported by a Grant-in-Aid for Young Scientist (B) from the Japan Society for the Promotion of Science (JSPS), No. 16K17660.

Appendix A
Correction for Blaze Function Variation and Normalization of Spectra

As Winn et al. (2004) showed, observations using HDS suffered from variation of the blaze function during the observations. The continuum profile is not important in our analysis, but it is useful to correct for this variation by subtracting the continuum of each spectrum. We used the first frame as the reference spectrum and compared the rest of the...
sensations by calculating the ratio of both spectra. By looking at
the ratio of all spectra, we found wavelength variations with
similar patterns for all orders, but these vary along the time of
the observation (see Figure 18). The ratio spectra were then
collapsed to remove any outliers. In order to avoid any residual
broad stellar absorption line mismatch in the ratio spectra, we
selected a 301 pixel smoothing window and applied smoothing
using PyAstronomy.pyasl.smooth with a flat window func-
tion. Each of the compared spectra was then divided by its
smoothened ratio spectra, resulting in a spectra with a blaze
function shared with the reference spectrum, while conserving
stellar line and telluric line strength variations. A spline
function was fitted to the reference spectrum using continuum
manually, and all spectra were divided by it to get the
normalized spectra.

Appendix B
SYSREM Algorithm

As in Tamuz et al. (2005), the aim is to find the two sets of
effective extinction coefficients (c) and air mass (a) that
optimally describe the atmospheric absorption in each
wavelength bin (i) of each frame (j). By taking the observed
air mass as the first input of a, we search for the optimal c that
minimizes

$$R_i^2 = \sum_j \frac{(r_{ij} - c_i a_j)^2}{\sigma_j^2},$$  \hspace{1cm} (4)

where \( \sigma \) is the uncertainty of the pixels \( ij \) calculated by taking
the root sum square of the standard deviations of its frame and
the wavelength bin. Then, \( c_i \) can be estimated from

$$c_i = \frac{\sum_i (r_{ij} a_j / \sigma_j^2)}{\sum_j (a_j^2 / \sigma_j^2)}.$$  \hspace{1cm} (5)

By using the estimated \( c_i \), we can find the “optimized air mass”
\( (a^{(1)}_j) \) that minimizes

$$R_j^2 = \sum_i \frac{(r_{ij} - c_i a_j)^2}{\sigma_j^2}$$  \hspace{1cm} (6)

by calculating

$$a^{(1)}_j = \frac{\sum_i (r_{ij} c_i / \sigma_j^2)}{\sum_i (c_i^2 / \sigma_j^2)}.$$  \hspace{1cm} (7)

By using the “optimized air mass,” the “optimized coefficient”
\( c^{(1)}_i \) can be calculated and by performing this “criss-cross”
iteration, the stable value of \( c^{(1)}_i, a^{(1)}_j \) can be found. The residual
can be calculated as

$$r^{(1)}_{ij} = r_{ij} - \hat{c}^{(1)}_i \hat{a}^{(1)}_j.$$  \hspace{1cm} (8)

At this point, the first systematic effect has been removed; then,
by performing a similar calculation to find the \( c^{(2)}_i, a^{(2)}_j \) that
minimize

$$R_i^2 = \sum_j \frac{(r^{(1)}_{ij} - c^{(2)}_i a^{(2)}_j)^2}{\sigma_j^2},$$  \hspace{1cm} (9)

the second and subsequent systematics can be calculated and
removed. Note that \( \hat{c}, \hat{a} \) does not actually represent the real
extinction coefficient and air mass even for the first iteration,
but a linear systematic effect that varies as a function of
wavelength and time (or frame number).

Appendix C
Cross-section of Molecules

The TiO line list from Plez (1998) was used, which include five
different isotopes with nine electronics systems and the
partition function that was published by Barklem & Collet
(2016). As Py4CATS only supports HITRAN- and GEISA-like
databases, instead of using its extract module, we used our
custom-built Python script to extract the TiO line list and wrote
them in HITRAN-like format, which then were used to
calculate the cross-sections line by line. The cross-section (k)
of each line is a product of the line strength (S) and a
normalized line profile function (g),

$$k(\nu; \dot{\nu}, S, \gamma) = S(T) \cdot g(\nu; \dot{\nu}, \gamma) \text{ with } \int_{-\infty}^{\infty} g(d\nu) = 1,$$  \hspace{1cm} (10)

where \( \gamma \) is the line-broadening half-width at half-maximum
(HWHM), \( \nu \) is the frequency, and \( \dot{\nu} \) is the line centroid
position. We modified lhh2x.py at the adjusting the line
parameter of the \( p \) and \( T \) sections to enable it to calculate the
line strength using other partition function databases, and to
include thermal (Doppler), natural, and van der Waals broad-
ening for TiO in the line profile calculations. The line strength
at temperature \( T \) (\( S(T) \)) is calculated by using Equation (1) in
Sharp & Burrows (2007). A Voigt function was used for the
line profile, which is defined as

$$K(x, y) = \frac{y}{\pi} \int_{-\infty}^{\infty} \frac{e^{-t^2}}{(x-t)^2 + y^2} dt,$$  \hspace{1cm} (11)

where \( x, y \) are defined as dimensionless variables in terms of
distance from the line centroid position, \( \nu - \dot{\nu} \), and the ratio of
the Lorentz and Gaussian HWHMs \( \gamma_L, \gamma_D \):

$$x = \sqrt{\ln 2} \frac{\nu - \dot{\nu}}{\gamma_D} \quad \text{and} \quad y = \sqrt{\ln 2} \frac{\gamma_L}{\gamma_D}.$$  \hspace{1cm} (12)

The thermal broadening is expressed with a Gaussian profile
\( g_D(\nu) \):

$$g_D(\nu) = \frac{1}{\gamma_D} \left( \frac{\ln 2}{\pi} \right)^{1/2} \exp \left[ -\ln 2 \frac{(\nu - \dot{\nu})^2}{\gamma_D^2} \right]$$  \hspace{1cm} (13)

with \( \gamma_D = \dot{\nu} \sqrt{\frac{2 \ln 2 k T}{m c^2}} \),

while natural and van der Waals broadening is expressed with a
Lorentz profile \( g_L(\nu) \):

$$g_L(\nu) = \frac{\gamma_L/\pi}{(\nu - \dot{\nu})^2 + \gamma_L^2},$$  \hspace{1cm} (14)
where \( k \) is Boltzmann’s constant, \( T \) is temperature, \( m \) is the mass of the molecular absorber, and \( c \) is the speed of light. \( \gamma_L \) is a sum of the van der Waals (\( \gamma_{LW} \)) and natural (\( \gamma_{LN} \)) line-broadening HWHMs,

\[
\gamma_L = \gamma_{LW} + \gamma_{LN}.
\]  

As there was no information available for the van der Waals line-broadening width of both molecules, we calculated it by following Sharp & Burrows (2007):

\[
\gamma_{LW} = \gamma_0 \frac{p}{p_0} \times \left( \frac{T_0}{T} \right)^n
\]

with

\[
\gamma_0 = \frac{1}{2} \left[ w_0 - \text{min}(J'', 30)w_1 \right],
\]

where \( J'' \) is the lower rotational quantum number of each energy transition, \( w_0 \) is the FWHM of a transition at 1 atm (\( p_0 \)) when \( J'' = 0 \), \( w_1 \) is a scale factor of the dependency of the broadening on \( J'' \), and as suggested in the paper we used \( w_0 = 0.1 \text{ cm}^{-1} \), \( w_1 = 0.002 \text{ cm}^{-1} \), and \( n = 0 \). The minimum criterion in Equation (17) means that the line broadening at \( J'' = 30 \) is used for larger \( J'' \) values. We used the formalism by Gray (1976) for the natural broadening width:

\[
\gamma_{LN} = \frac{0.222 \, \rho^2}{4\pi c}.
\]

ORCID iDs

Stevenus K. Nugroho @ https://orcid.org/0000-0003-4698-6285

Hajime Kawahara @ https://orcid.org/0000-0003-3309-9134

Kento Masuda @ https://orcid.org/0000-0003-1298-9699

Akito Tajitsu @ https://orcid.org/0000-0001-8813-9338

References

Barklem, P. S., & Collet, R. 2016, A&A, 588, A96

Birkby, J. L., de Kok, R. J., Brogi, M., et al. 2013, MNRAS, 436, L35

Birkby, J. L., de Kok, R. J., Brogi, M., Schwarz, H., & Snellen, I. A. G. 2017, AJ, 153, 138

Brogi, M., de Kok, R. J., Albrecht, S., et al. 2016, ApJ, 817, 106

Brogi, M., Line, M., Bean, J., Désert, J.-M., & Schwarz, H. 2017, ApJL, 839, L2

Brogi, M., Snellen, I. A. G., de Kok, R. J., et al. 2013, ApJ, 767, 27

Burrows, A., Hubbard, W. B., Lunine, J. I., & Liebert, J. 2001, RVMP, 73, 719

Burrows, A., & Sharp, C. M. 1999, ApJ, 512, 843

Coelho, P. R. T. 2014, MNRAS, 440, 1027

Collier Cameron, A., Guenther, E., Smalley, B., et al. 2010, MNRAS, 407, 507

Collier Cameron, A., Pollacco, D., Street, R. A., et al. 2006, MNRAS, 373, 799

Crossfield, I. J. M., Barman, T., & Hansen, B. M. S. 2011, ApJ, 736, 132

de Kok, R. J., Brogi, M., Snellen, I. A. G., et al. 2013, A&A, 554, A82

Diamond-Lowe, H., Stevenson, K. B., Bean, J. L., Line, M. R., & Fortney, J. J. 2014, ApJ, 796, 66

Esteves, L. J., de Mooij, E. J. W., Jayawardhana, R., Watson, C., & de Kok, R. 2017, AJ, 153, 268

Evans, T. M., Sing, D. K., Kataria, T., et al. 2017, Natur, 548, 58

Evans, T. M., Sing, D. K., Wakeford, H. R., et al. 2016, ApJL, 822, L4

Fortney, J. J., Lodders, K., Marley, M. S., & Freedman, R. S. 2008, ApJ, 678, 1419

Gontcharov, G. A. 2006, A&AT, 25, 145

Gray, D. F. 1976, The Observation and Analysis of Stellar Photospheres (Cambridge: Cambridge Univ. Press)

Hansen, C. J., Schwartz, J. C., & Cowan, N. B. 2014, MNRAS, 444, 3632

Haynes, K., Mandell, A. M., Madhusudhan, N., Deming, D., & Knutson, H. 2015, ApJ, 806, 146

Hoeijmakers, H. J., de Kok, R. J., Snellen, I. A. G., et al. 2015, A&A, 575, A20

Hubeny, I., Burrows, A., & Sudarsky, D. 2003, ApJ, 594, 1011

Johnson, M. C., Cochran, W. D., Collier Cameron, A., & Bayliss, D. 2015, ApJL, 810, L23

Kaeufl, H.-U., Ballester, P., Biereichel, P., et al. 2004, Proc. SPIE, 5492, 1218

Kawahara, H. 2012, ApJL, 760, L13

Kawahara, H., & Hirano, T. 2014, arXiv:1409.5740

Knutson, H. A., Charbonneau, D., Allen, L. E., Burrows, A., & Megeath, S. T. 2008, ApJ, 673, 526

Knutson, H. A., Howard, A. W., & Isaacson, H. 2010, ApJ, 720, 1569

Kotani, T., Tamura, M., Suto, H., et al. 2014, Proc. SPIE, 9147, 914714

Kovács, G., Kovács, T., & Hartman, J. D. 2013, A&A, 553, A44

Mazeh, T., Tamuz, O., & Zucker, S. 2007, in ASP Conf. Ser. 366, Transiting Extrapolar Planets Workshop, ed. C. Afonso, D. Welsh, & T. Henning (San Francisco, CA: ASP), 119

Narita, N., Suto, Y., Winn, J. N., et al. 2005, PASJ, 57, 471

Noguchi, K., Aoki, W., Kawanomoto, S., et al. 2002, PASJ, 54, 855

Ott, A., Alonso, R., Bonomo, A. S., et al. 2010, MNRAS, 404, L99

Plez, B. 1998, A&A, 337, 495

Schwarz, H., Brogi, M., de Kok, R., Birkby, J., & Snellen, I. 2015, A&A, 576, A111

Sedaghati, E., Boffin, H. M. J., MacDonald, R. J., et al. 2017, Natur, 549, 238

Sharp, C. M., & Burrows, A. 2007, ApJS, 168, 140

Smith, A. M. S., Anderson, D. R., MacDonald, R. J., et al. 2017, Natur, 549, 238

Snellen, I. A. G., de Kok, R., Birkby, J. L., et al. 2015, A&A, 576, A59

Snellen, I. A. G., Albrecht, S., de Mooij, E. J. W., & Le Poole, R. S. 2008, A&A, 487, 357

Snellen, I. A. G., Brandl, B. R., de Kok, R., et al. 2014, Natur, 509, 63

Snellen, I. A. G., de Kok, R. J., de Mooij, E. J. W., & Albrecht, S. 2010, Natur, 465, 1049

Spiegel, D. S., Silverio, K., & Burrows, A. 2009, ApJ, 699, 1487

Tajitsu, A., Aoki, W., Kawanomoto, S., & Narita, N. 2010, PNAOJ, 13, 1

Tajitsu, A., Aoki, W., & Yamamuro, T. 2010, PASJ, 62, 1700

Tamuz, O., Mazeh, T., & Zucker, S. 2005, MNRAS, 356, 1466

von Essen, C., Mallonn, M., Albrecht, S., et al. 2015, A&A, 584, A75

Winn, J. N., Suto, Y., Turner, E. L., et al. 2004, PASJ, 56, 615

Zellem, R. T., Lewis, N. K., Knutson, H. A., et al. 2014, ApJ, 790, 53

Akito Tajitsu