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1 **Optical Properties of Organic Hazes in Water-rich Exoplanet Atmospheres:**
2 **Implications for Observations with *JWST***

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16 ***JWST* has begun its scientific mission, which includes the atmospheric**
17 **characterization of transiting exoplanets. Some of the first exoplanets to be observed**
18 **by *JWST* have equilibrium temperatures below 1000 K, which is a regime where**
19 **photochemical hazes are expected to form. The optical properties of these hazes,**
20 **which controls how they interact with light, are critical for interpreting exoplanet**
21 **observations, but relevant data are not available. Here we measure the optical**
22 **properties of organic haze analogues generated in water-rich exoplanet atmosphere**
23 **experiments. We report optical constants (0.4 to 28.6 μm) of organic hazes for current**
24 **and future observational and modeling efforts covering the entire wavelength range**
25 **of *JWST* instrumentation and a large part of *Hubble*. We use these optical constants**
26 **to generate hazy model atmospheric spectra. The synthetic spectra show that**
27 **differences in haze optical constants have a detectable effect on the spectra, impacting**
28 **our interpretation of exoplanet observations. This study emphasizes the need to**
29 **investigate the optical properties of hazes formed in different exoplanet atmospheres,**
30 **and establishes a practical procedure to determine such properties.**

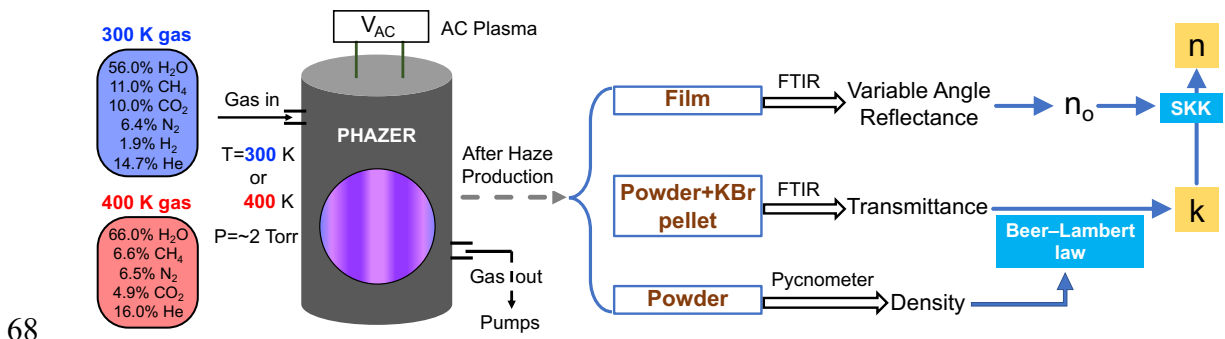
31 **1. INTRODUCTION**

32 Observations¹⁻⁶ indicate that many exoplanets could possess cloud and haze particles in
33 their atmospheres and that these particles impact observed spectra. Recent modeling^{7,8} and
34 laboratory studies⁹⁻¹² suggest that organic haze particles are produced photochemically in
35 temperate (<1000 K) exoplanet atmospheres, which are prime targets of observations for
36 assessing habitability and searching for biosignatures beyond the Solar System. However,
37 many exoplanets in this temperature range (including super-Earths and mini-Neptunes)
38 have no Solar System analogs. The compositions and properties of organic hazes might be
39 very distinct from what we know for Solar System bodies. These organic hazes can alter
40 the transmission, emission, and reflected light spectra of exoplanets.^{8,13} The optical
41 properties of these hazes are essential to interpret exoplanet spectroscopic data and
42 understand of their atmospheres.

43 Because the optical properties of exoplanet organic hazes are not yet known, the optical
44 constants of Titan-like hazes (produced with 10% CH₄ in N₂) from Khare et al. (1984)¹⁴
45 and of soots (carbonaceous particles formed from incomplete combustion of
46 hydrocarbons)¹⁵ are widely used to generate models and interpret observations.^{8,16,17} In
47 reality, the organic hazes formed in diverse atmospheres have a variety of compositions¹⁸
48 and therefore diverse optical properties. The optical properties of Titan-like hazes or soots
49 simply cannot represent the wide variety of atmospheric hazes we anticipate on
50 exoplanets.⁹⁻¹² It is therefore necessary to measure the optical properties of organic hazes
51 formed over a broad range of atmospheric conditions, given that JWST has begun to deliver
52 unprecedented observations of various exoplanets.⁶

53 Exoplanets are expected to exhibit a wide diversity of atmospheric compositions. The
54 signature of water is particularly sought on potentially habitable exoplanets because water
55 is a key element for life on Earth. For example, water vapor has been detected in the
56 atmosphere of a non-terrestrial exoplanet (K2-18 b) in the habitable zone.^{19,20} Modeling
57 studies²¹⁻²⁵ suggest that water worlds could be very common among low mass exoplanets

58 and there might be many water-rich atmospheres. Previous laboratory studies^{9,10,18} have
 59 shown that water-rich atmospheres are likely to result in organic haze formation. Opacity
 60 from organic hazes can mask spectral features from water and other gases.^{2,3,26,27} Here we
 61 measure the density and the optical properties of hazes analogous to those produced in
 62 temperate water-rich atmospheres. Their optical constants (the real refractive indices, n ,
 63 and the extinction coefficients, k) are derived from 0.4 to 28.6 μm , covering optical
 64 wavelengths accessible with *Hubble* and ground-based facilities and the entire *JWST*
 65 wavelength range. Fig. 1 summarizes our experimental setup, the initial gas compositions
 66 and conditions, the measurements, and the analytical method of this study (for detailed
 67 information, see Methods).



68
 69 **Fig. 1.** Simplified schematic of the experimental setup, the simulated atmospheric
 70 compositions and conditions, the measurements, and the analytical method for the current
 71 study. Two haze analogues are produced with the PHAZER chamber by exposing the gas
 72 mixture (300 K or 400 K) to AC plasma energy source. These two gas mixtures represent
 73 the equilibrium compositions for atmospheres with 1000 times solar metallicity at 300 and
 74 400 K, which are guided from chemical-equilibrium calculations (see Methods). The high
 75 haze production rate in these two gas mixtures¹⁰ allows further analysis of the properties
 76 of the resulted haze particles. The density of the haze analogues is determined using a gas
 77 pycnometer, and their transmittance and reflectance spectra are measured with a Fourier
 78 transform infrared (FTIR) spectrometer. The extinction coefficients (k) are calculated
 79 based on the Beer-Lambert law, and the real refractive indices (n) are derived using the
 80 subtractive Kramers-Kronig (SKK) relation between n and k .

81 **2. RESULTS**

82 *2.1. Density of Exoplanet Haze Analogues*

83 The density of organic haze particles is an important property that impacts aerosol
84 microphysics processes (coagulation, transport, and sedimentation) in exoplanet
85 atmospheres. However, prior to this study the particle density was unknown due to lack of
86 observational and experimental constraints. The haze mass density is often assumed to be
87 1 g cm^{-3} in many microphysics models²⁸⁻³⁰, which is lower than the density we measured
88 here. Our measurements here provide the first experimental constraints on the density of
89 organic haze particles formed in water-rich exoplanet atmospheres, enabling realistic
90 analysis and interpretation of observations of such exoplanets.

91 The measured densities are 1.328 and 1.262 g cm^{-3} (measurement uncertainties $<1\%$) for
92 the haze analogues from the simulated exoplanet atmospheres at 300 and 400 K ,
93 respectively. Their densities are lower than the haze analogues produced with the PHAZER
94 chamber for icy bodies (1.35 - 1.43 g cm^{-3} for Titan, Triton, and Pluto haze analogues) in
95 our Solar System.³¹ The density differences reflect their distinct chemical compositions.
96 Elemental analysis has shown that the two haze analogues for exoplanets have higher
97 oxygen ($>15\%$ compared to $<10\%$) but lower nitrogen ($\sim 22\%$ compared to $\sim 40\%$) contents
98 relative to haze analogues for Titan, Triton and Pluto.^{18,32} Besides the differences in
99 elemental compositions, the chemical structures in each haze analogue, such as their
100 molecular weight, polarity, and degree of unsaturation, also affect their density.

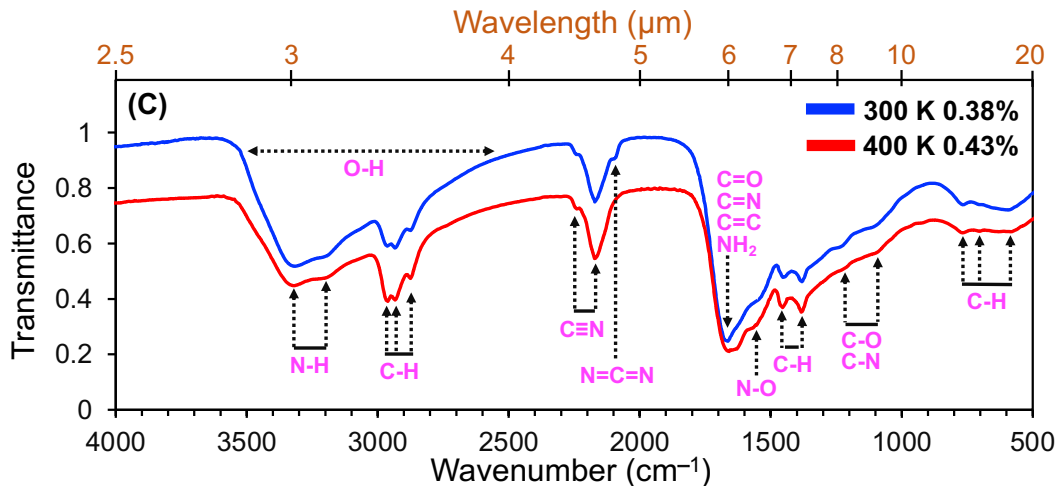
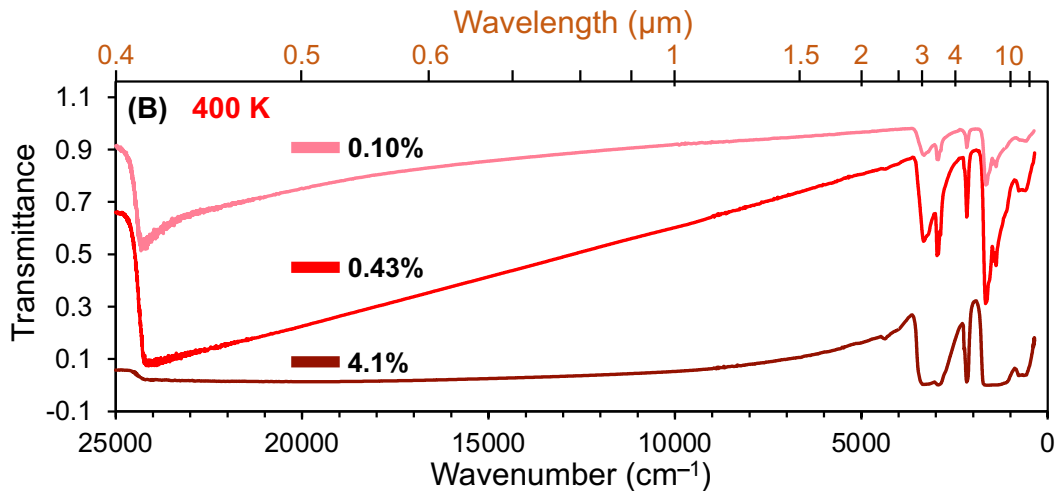
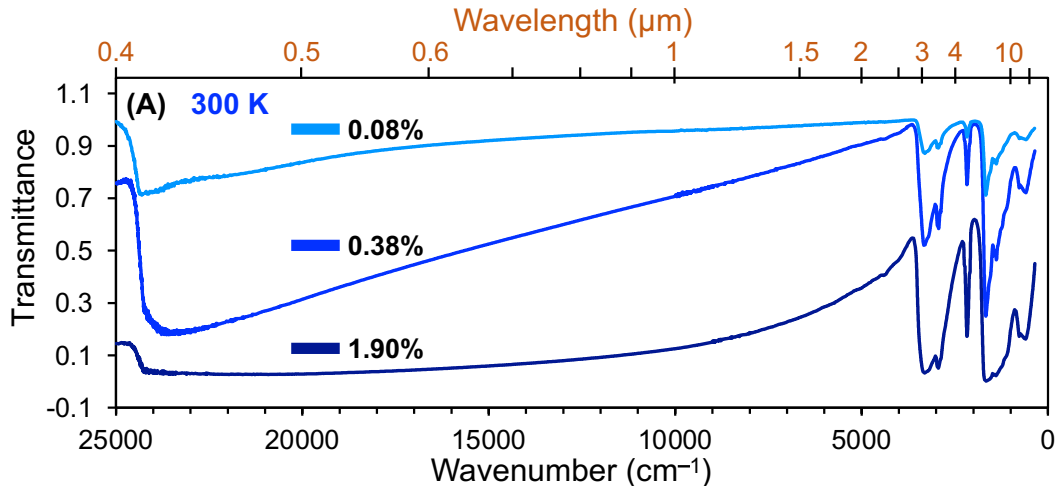
101 *2.2. Transmittance of Exoplanet Haze Analogues and their Functional Groups*

102 Exoplanet atmospheric transmission observations, obtained as the planet passes in front of
103 host star, will be shaped by any hazes in the planet's atmosphere. Fig. 2 shows the
104 transmittance of the two exoplanet haze analogues (300 and 400 K samples). For each
105 sample, the transmittance spectra are obtained at three different concentrations in

106 potassium bromide (KBr) to capture both strong and weak absorption features. KBr is a
107 typical carrier (as pellet or disk) for spectroscopy measurements because it is optically
108 transparent from ultraviolet (0.22 μm) to far IR ($\sim 30 \mu\text{m}$). As shown in Fig. 2, the general
109 spectral shape and features are similar at both temperatures. They both have an absorption
110 feature at 0.42 μm , suggesting that the samples contain aromatic compounds and/or
111 unsaturated species with conjugated pi bonds.^{33,34} The spectra are featureless from 0.5 to
112 2.5 μm but the absorption becomes weaker as the wavelength increases. Many absorption
113 features appear from 2.5 to 20 μm due to bond vibrations of various organic functional
114 groups in the haze analogues.

115 We expand this region in Fig. 2C to show the characteristic frequencies of different bonds.
116 Fig. 2C identifies the bonds responsible for each spectral feature, including the
117 characteristic absorptions of O–H, N–H, C–H, C \equiv N, –N=C=N–, C=O, C=N, C=C, N–O,
118 C–O, and C–N bonds.^{35,36} Table 1 summarizes the vibration modes of these bonds and their
119 peak intensities. The absorption feature at 3500–2500 cm^{-1} (2.86–4.00 μm) is due to O–H
120 bond stretching. This strong, broad feature indicates the predominance of alcohols (3500–
121 3200 cm^{-1}) and carbonic acids (3300–2500 cm^{-1}) in the haze analogues. The stretching of
122 N–H (3350–3300 and 3215–3190 cm^{-1}) and C–H (2965, 2933, 2875 cm^{-1}) bonds is present
123 in this range as well but appears as relatively sharp peaks. Other absorption features in the
124 spectra indicate the presence of nitriles, aromatics, and unsaturated and saturated organics
125 in both the 300 and 400 K haze analogues. A small amount of carbodiimide compounds (–
126 N=C=N–, $\sim 2100 \text{cm}^{-1}$) are only present in the 300 K haze sample, probably because lower
127 temperature promotes carbodiimide formation from cyanamide.³⁷ Compared to Titan-like
128 hazes^{38,39}, the exoplanet haze analogues in this study have obvious compositional
129 differences, which include various oxygen-containing groups. This is not unexpected
130 because there are two major oxygen-containing gases (H_2O and CO_2) in the initial
131 atmospheres. The presence of oxygen-containing groups in the exoplanet haze analogues
132 is supported by other analyses. Elemental analysis shows that these two haze analogues

133 have large oxygen contents (15% or 17% in mass), and high-resolution mass spectra reveal
 134 many oxygen-containing molecules in these samples.¹⁸ The compositional difference leads
 135 to distinctive optical properties of the exoplanet haze analogues.



136

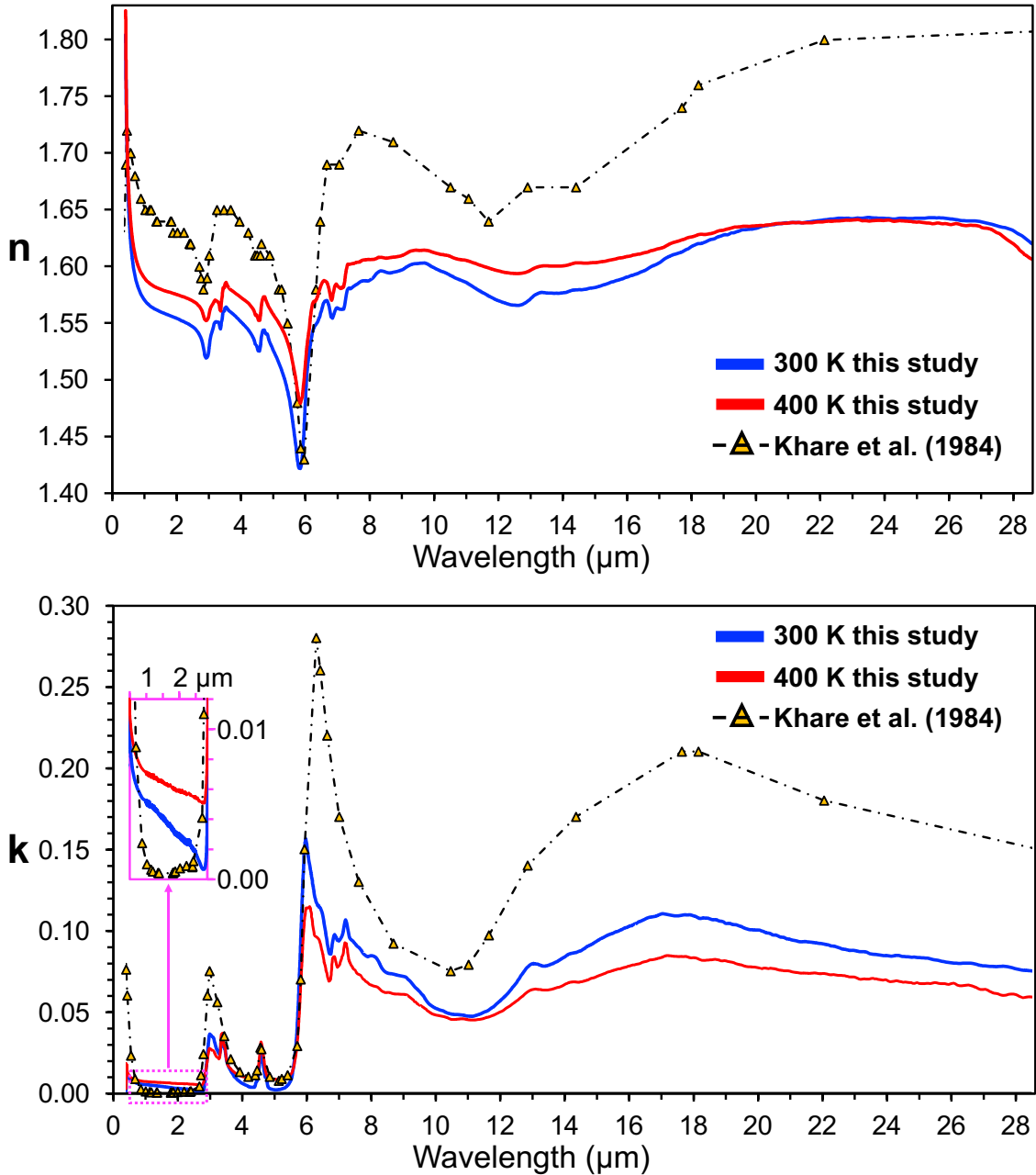
137 **Fig. 2.** The transmittance spectra of two exoplanet haze analogues formed in water-rich
 138 atmospheres at 300 K (A) and 400 K (B). The lines with different shades of color show the
 139 spectra of the samples with different concentrations in KBr (lighter color indicates lower
 140 concentration and darker indicates higher). The sample is mixed with KBr, and the
 141 percentage concentration is by mass. The transmittance spectra are obtained at different
 142 concentrations to capture both strong and weak absorption features in the samples. Panel
 143 C is the expansion of two spectra from panels A (0.38% of the 300 K sample) and B (0.43%
 144 of the 400 K sample) from 2.5 to 20 μm to show the absorption features of various
 145 functional groups. Different bonds are labeled in the figure near their absorption features.
 146

147 **Table 1.** Functional group assignments to characteristic absorption frequencies of two
 148 exoplanet haze analogues as observed in the transmittance spectra (Fig. 2)

Frequency (ν) cm^{-1}	Wavelength (λ) μm	Functional group	Intensity
3500-2500	2.86-4.00	-O-H stretching, in alcohols and carbonic acids	strong, broad
3350-3300	2.98-3.03	-NH ₂ or -NH- stretching	strong
3215-3190	3.11-3.13	-NH ₂ stretching or overtone of NH ₂ bending	strong
2965	3.37	-CH ₃ asymmetric stretching	strong, sharp
2933	3.41	-CH ₂ - asymmetric stretching	strong, sharp
2875	3.48	-CH ₃ symmetric stretching	strong, sharp
2244-2232	4.46-4.48	-C \equiv N or R-C=C-R stretching	medium, shoulder
2172	4.60	Conjugated -C \equiv N stretching	strong, sharp
2108-2094	4.74-4.77	-N=C=N- stretching	medium, shoulder
1680-1626	5.95-6.15	C=O, C=N, C=C stretching or -NH ₂ scissors bending	very strong
1580-1540	6.33-6.49	C=C stretching (aromatic) or N-O stretching (nitro)	medium, shoulder
1462-1450	6.84-6.90	sp ³ C-H bending	strong, sharp
1386-1378	7.21-7.26	sp ³ C-H bending or aldehydic C-H bending	strong, sharp
1247-1224	8.02-8.17	C-O or C-N stretching (aromatic)	weak, shoulder
1126-1104	8.88-9.06	C-O or C-N stretching (aliphatic)	weak, shoulder
775-762	12.9-13.12	sp ² C-H bending	medium
714-701	14.0-14.26	sp ² C-H bending	medium
612-584	16.34-17.12	sp ² C-H bending	medium

149 *2.3. Optical Constants of Exoplanet Haze Analogues*

150 Optical constants for hazes can be used incorporate their features into theoretical spectra
151 and for comparisons with retrieved values from observations. Fig. 3 shows the optical
152 constants of two exoplanet haze analogues (300 and 400 K). The real refractive indices (n)
153 are in the range between 1.43 and 1.82 for both samples, and the extinction coefficients (k)
154 vary in a broad range from $\sim 10^{-3}$ to 10^{-1} . The detailed data and their uncertainties can be
155 found in Supplementary Information (Table S1). The uncertainties of the k values are
156 estimated by considering the uncertainties of the transmittance measurements, the
157 thickness calculations, and the average relative standard deviation of k values obtained for
158 the samples at three different concentrations. For the n values, the uncertainties are
159 determined from the error propagations of the uncertainty of n_0 at the anchor point and the
160 integration of the k values. The uncertainties for the k values are about 1-4% at longer
161 wavelengths ($>2.9 \mu\text{m}$) where the k values are larger than 0.01, but increase up to 9% at
162 shorter wavelengths (0.4 to $2.9 \mu\text{m}$) where the k values are smaller than 0.01. The
163 determined n values have small uncertainties (3-4%) across the measured wavelength range
164 because of the accuracy of the n_0 (uncertainty less than 1%) and the integration of the k
165 values over the entire wavelength range. The n and k values of the two haze analogues (300
166 and 400 K) are similar in general and share many fine-scale features. Over most of the
167 measured wavelength range, the 300 K sample has slightly lower n values but slightly
168 higher k values relative to the 400 K sample. This could be caused by differences in their
169 chemical compositions. For example, the 300 K sample has higher extinction coefficient
170 at $\sim 3 \mu\text{m}$, indicating that it contains more N-H bonds. This is consistent with the elemental
171 analysis that shows the 300 K sample has higher nitrogen content than the 400 K sample
172 (27% vs 21%).¹⁸ In addition, the higher extinction coefficients at 5.9-6.5 μm suggest that
173 there are more double bonds in the 300 K sample.



174

175 **Fig. 3.** Optical constants of two exoplanet haze analogues along with those of Titan-like
 176 hazes from Khare et al (1984): (A) the real refractive indices (n), and (B) the extinction
 177 coefficients (k) as function of wavelength (0.4 to 28.6 μm). The inset of (B) shows the
 178 difference of k values between this study and the one from Khare et al (1984), when k
 179 is smaller than 0.01 from 0.5 to 2.9 μm .

180

181 The optical constants of Titan-like hazes from Khare et al. (1984)¹⁴ are also plotted in Fig.

182 3 for comparison. Due to its extensive spectral coverage (from soft X-ray, 0.025 μm , to

183 microwave frequencies, 1000 μm), the optical constants from Khare et al. (1984)¹⁴ are
184 widely used in atmospheric modeling and observation interpretations for both Solar System
185 bodies (Titan⁴⁰, Triton⁴¹, and Pluto⁴²) and many exoplanets.^{30,31,43} However, the haze
186 analogues used in Khare et al. (1984)¹⁴ for the optical measurements were produced with
187 DC plasma discharge in $\text{N}_2/\text{CH}_4 = 90/10$ gas mixture at 0.2 mbar, with the purpose of
188 simulating haze particles formed in Titan's upper atmosphere.

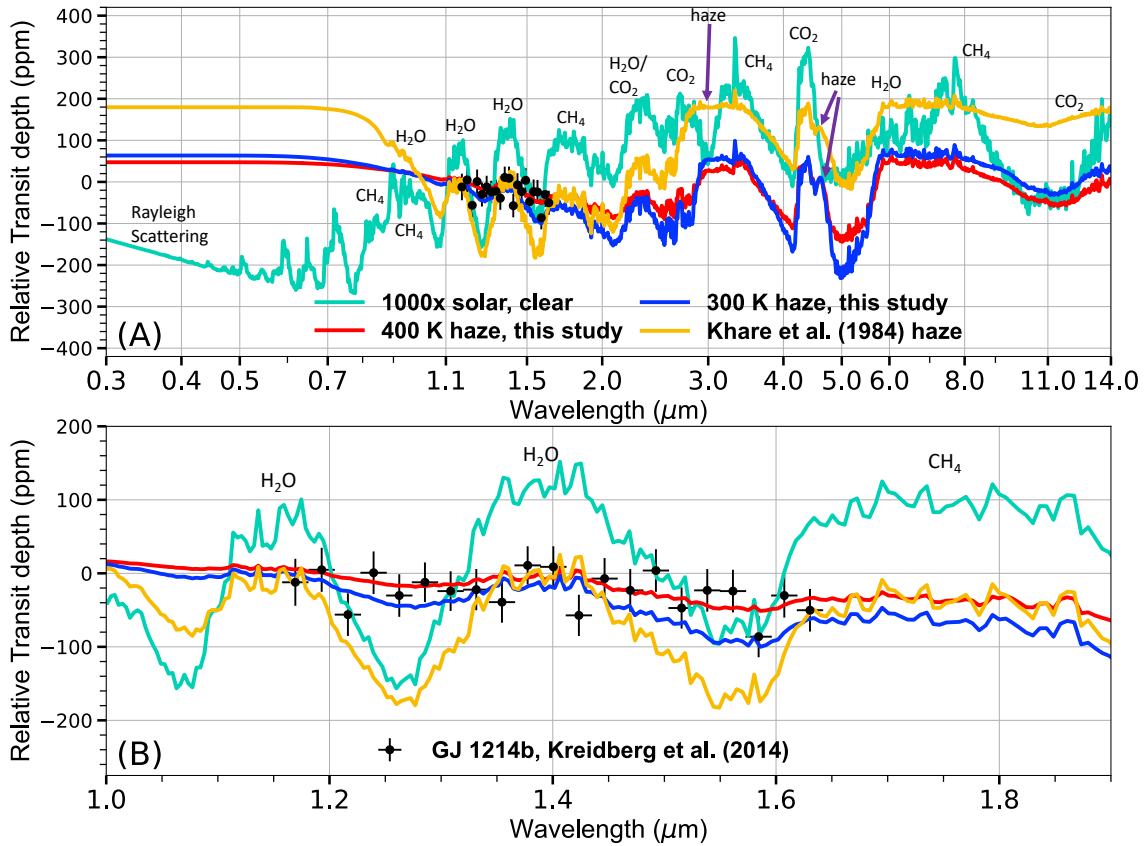
189 As shown in Fig. 3, the general trend of the optical constants of two exoplanet haze
190 analogues in this study is similar to that of the Titan-like hazes from Khare et al. (1984)¹⁴
191 because of the organic nature of these materials. However, our n and k values are
192 substantially smaller than those of Khare et al. (1984)¹⁴ over most of the measured
193 wavelength range. Both of our two samples have smaller n values than the Titan-like hazes
194 from Khare et al. (1984)¹⁴ except at 5.8-6.2 μm where their n values are similar to those of
195 our 300 K sample. The k values from Khare et al. (1984)¹⁴ at 0.4-0.6 μm , ~ 3 μm , and above
196 6 μm are about two times greater than our k values; they are comparable to the k values of
197 our 400 K sample from 3.4 to 5.8 μm ; but they are smaller than our k values in the short
198 wavelength region (0.7-2.6 μm). Besides the differences of the absolute n and k values, the
199 data from Khare et al. (1984)¹⁴ has fewer features than our values mainly due to two reasons.
200 First, the spectral measurements in Khare et al. (1984)¹⁴ were done at very low resolution,
201 especially over the longer wavelengths (6-28.6 μm); second, the compositions are distinct
202 between our samples and those in Khare et al. (1984). The low-resolution can lead to fine
203 features not being resolvable (such as those from 6-10 μm), and the compositional
204 difference may cause some features to be weaker or absent (such as those at 3-3.5 μm).
205 The higher spectral resolution of the current study reveals new spectral features that may
206 enable measurements of haze composition, rather than just haze detection. Nonetheless, the
207 differences in the absolute values and the features can have consequential impacts on
208 atmospheric modeling and observational interpretation of exoplanets.

209 *2.4. Effect of New Optical Properties of Exoplanetary Hazes on Atmospheric Transmission*
210 *Spectra*

211 We next briefly explore the effects of these newly derived exoplanet haze optical properties
212 on transmission spectra for a representative exoplanet atmosphere. Since the experiments
213 were run for hazy, water-rich atmospheres, we choose the parameters of the well-studied,
214 likely aerosol-laden exoplanet GJ 1214 b as a reasonable example planet to demonstrate
215 how our new optical properties would affect observations. GJ 1214 b has a mass of $8.17 \pm$
216 $0.43 M_{\oplus}$, a radius of $2.742 \pm 0.05 R_{\oplus}$, and an equilibrium temperature of 596 K.⁴⁴ The
217 planet’s mass and radius suggest its bulk density could be consistent with a hydrogen-rich
218 atmosphere, or a steam atmosphere with a significant hydrogen/helium fraction⁴⁴ as in our
219 experiments. The temperature is sufficiently warm that water should not condense out of
220 the upper atmosphere. Observations with *Hubble* show its atmosphere has a featureless
221 transmission spectrum from 1.1 to 1.7 microns, which could be indicative of a high altitude
222 (\sim mbar) haze layer.¹ The incident UV flux is expected to drive significant photochemistry
223 and potentially haze formation.^{45,46}

224 Fig. 4 shows the synthetic spectra of a water-rich atmosphere reflecting the initial gas
225 composition from the experiments at 400 K around a GJ 1214 b-like planet with the effects
226 of a haze layer. We use the open-source aerosol modeling code *Virga*^{47,48} and the open-
227 source radiative transfer suite *PICASO*⁴⁹ to compute Mie properties for our hazes and
228 implement them into a synthetic transmission spectrum model of an exoplanetary
229 atmosphere (for detailed information about the haze modeling and generating the synthetic
230 spectra, see Methods). We show spectra based on our newly derived optical properties for
231 300 and 400 K water-rich atmospheric hazes and for the commonly used Titan-like haze
232 of Khare et al. (1984)¹⁴. Our aim in this work was to isolate the effect of the different haze
233 optical properties on the atmospheric transmission spectra rather than perform a full model
234 parameter study, and so we held all other haze parameters (e.g., particle size distribution,
235 number density, vertical mixing) fixed. Interpretation of actual atmospheric spectral data

236 would require a full investigation into all these variables but is beyond the scope of this
 237 work.



238
 239 **Fig. 4.** Model spectra of a water-rich atmosphere around a GJ 1214 b -like planet, showing
 240 the effect of our newly measured haze optical properties. We also show the existing *Hubble*
 241 data of GJ 1214 b (Kreidberg et al. 2014)¹. All spectra have been normalized by subtracting
 242 the mean of each transit depth from the spectrum, to better show the relative sizes of
 243 absorption features. The top panel (A) shows the spectra of our modeled atmospheres from
 244 0.4 to 14 microns; bottom panel (B) shows our model atmospheres focused on *Hubble*
 245 Wide Field Camera 3/G141 instrument wavelengths. In teal, we show models of clear
 246 atmospheres with the laboratory atmospheric composition. Orange lines show hazy models
 247 generated using the optical properties for Titan-like hazes as measured by Khare et al.
 248 (1984). Red and blue lines show models generated using our newly derived optical
 249 properties for hazes made from 400 and 300 K water-rich atmospheres, respectively. The
 250 molecules and/or hazes responsible for the atmospheric features are indicated in each plot.
 251 **Given the same other atmospheric assumptions, the presence of our newly measured**
 252 **hazes would be differentiable from a Titan-like haze with observations from existing**
 253 **space-based observatories like *Hubble* and *JWST*, as with the GJ 1214 b data shown**
 254 **here.**
 255

256 Throughout the spectrum, the values of n and k between our newly measured water-rich
257 derived hazes and those of the Titan-like hazes¹⁴ show similar behavior but at different
258 intensities, as shown in Fig. 3. As such, all the hazy synthetic spectra we show in Fig. 4
259 mute the gaseous spectral features of the atmosphere, but to differing extents depending on
260 the optical properties assumed for the haze particles. Notably, the Khare Titan-like hazes
261 more heavily mute the atmospheric spectral features longward of 3.0 μm , while our water-
262 rich hazes more heavily mute the atmospheric spectrum between 0.7 and 2.5 μm — that is,
263 the wavelength region of focus for most *Hubble* exoplanet studies. In particular, the Titan-
264 like hazes more strongly absorb at $\sim 3 \mu\text{m}$ and $\sim 6 \mu\text{m}$, which probe functional groups due
265 to amine (N-H) as well as carbon- and nitrogen-bearing (C=C, C=N, NH₂) bonds. The
266 transit depth differences between haze models range from ~ 100 ppm in the mid-IR to ~ 150
267 ppm in the visible and near-IR, all of which are well within the sensitivity of *JWST* and
268 *Hubble* measurements,^{1,51-55} though this result relies on the same particle size distributions
269 for the different kinds of hazes.

270 Additionally, the strength of the Rayleigh scattering slope from the visible towards the
271 near-UV is enhanced by all hazes, though the Titan-like hazes absorb more strongly
272 because of their larger k over the shortest wavelengths (0.4 to 0.7 μm). The difference
273 between the visible-UV slopes of Titan-like and water-rich derived hazes is ~ 150 ppm for
274 our modeled atmospheres. Smaller particles would enhance the variation between the
275 visible-UV slopes (see Extended Data Fig. 3). Such differences are within the precision of
276 *Hubble*'s WFC3/UVIS instrument, which covers 0.2 to 0.8 μm . Since we have explicitly
277 modeled the same haze particle size distributions and number densities for each set of
278 optical properties, these differences here stem purely from the stronger absorption by the
279 Titan-like haze over these wavelengths. In other words, using the optical properties from
280 this study or from Khare et al. (1984)¹⁴ to fit spectra from real observations would result in
281 different inferred particle sizes and number densities for the same atmosphere to achieve
282 the same scattering slope.

283 Most interestingly, our water-rich derived hazes almost completely mute the atmospheric
284 spectrum over the HST WFC3/G141 bandpass, but the Titan-like haze of Khare et al.
285 (1984)¹⁴ allows the water and methane atmospheric features to peek through from 1 to 2
286 μm because its k values are an order of magnitude lower in the NIR. This results in our
287 water-rich hazes providing a better match to the existing GJ 1214 b data from *Hubble*¹
288 compared to the Khare et al. (1984)¹⁴ Titan-like hazes for the same abundance of haze mass
289 loading. Both sets of haze optical properties allow atmospheric features to peek through at
290 redder wavelengths which are covered by *JWST*. The size of these atmospheric features at
291 longer wavelengths, even muted by haze, is still well within the precision of *JWST*
292 measurement. Future model development and modeling studies, beyond the scope of this
293 work, are needed to fully assess how vertical mixing and sedimentation of haze layers with
294 these optical properties influence atmospheric spectra.

295 3. DISCUSSION

296 So far, the optical constants of the Titan-like hazes by Khare et al. (1984)¹⁴ and various
297 soots¹⁵ have served as the only source for optical properties of organic haze in exoplanet
298 atmospheres. Our study provides optical constants (0.4 to 28.6 μm) of organic hazes
299 photochemically produced in water-rich exoplanet atmospheres. The optical constants of
300 our water-rich derived exoplanet hazes differ from those of the Titan-like hazes¹⁴, therefore
301 affecting transmission, thermal emission, and reflected light spectra of exoplanets to
302 different extents. When interpreting actual observations of exoplanets, using different
303 optical constants of hazes can lead to different conclusions; in some cases, using
304 inapplicable optical constants may lead to misinterpretations. Such misinterpretations
305 could include incorrect atmospheric abundances of key species such as water and
306 methane^{56,57}, or incorrect aerosol particle sizes and extents³⁰, which could then further
307 affect the temperature structure¹⁷ and thus the inferred dynamics and climate feedbacks
308 within an atmosphere.⁵⁸

309 JWST has an unprecedented capability to detect faint chemical signatures in exoplanet
310 atmospheres and is set to observe a wide variety of exoplanet types. The haze particles
311 formed in those exoplanet atmospheres are likely to have different compositions, which
312 would then have distinct optical properties. The optical properties of different hazes are
313 essential to interpreting observations, but we should be cautious when applying the existing
314 haze optical constants to different types of exoplanets. In addition, the optical constant data
315 of different hazes are necessary input parameters for atmospheric modeling of various
316 exoplanets to understand their physical and chemical processes (i.e., their temperature
317 structures, climates, etc.). The two sets of optical constants reported here are applicable for
318 temperate water-rich exoplanet atmospheres and can be used for current and future
319 observational and modeling efforts of such atmospheres. More laboratory work is needed
320 to determine optical constants of haze analogues formed in various exoplanet atmospheric
321 regimes. This study demonstrates a feasible avenue to determine such properties in the
322 future.

323 **4. METHODS**

324 *4.1 Production of Haze Analogues*

325 The exoplanet haze analogues are produced using the Planetary Haze Research (PHAZER)
326 experimental setup at Johns Hopkins University.³¹ The detailed experimental procedure
327 has been described previously.⁹⁻¹² This study uses haze analogues produced in the two
328 water-rich atmospheres from our previous investigations.^{9,10,18} The initial gas mixtures for
329 our experiments are guided by the calculations from the chemical-equilibrium models of
330 Moses et al. (2013).⁵⁹ Photochemical hazes are expected to play an important role in the
331 atmospheres of exoplanets with equilibrium temperature below 1000 K, especially those
332 planets with enhanced metallicities or enhanced C/O ratios.^{7,9,10} The detailed compositions
333 of actual exoplanet atmospheres have not yet been measured well, so we resort to chemical
334 equilibrium calculations⁵⁹ to guide our experiments. The equilibrium atmospheric

335 compositions provide a reasonable starting point to investigate the photochemical
336 processes in the atmospheres of super-Earths and mini-Neptunes with higher metallicity.
337 In our previous studies⁹⁻¹², we explored atmospheres with a range of metallicities (100×,
338 1000×, and 10,000× solar metallicity) and equilibrium temperatures (300, 400, 600, and
339 800 K). The two water-rich atmospheres represent the equilibrium compositions for
340 atmospheres with 1000× solar metallicity at 300 and 400 K. These two atmospheres
341 produce haze at a higher rate than the other cases¹⁰, which allows further analysis of the
342 properties of the resulting haze particles.

343 Here, we briefly recount the production procedure. Gas mixtures, excluding water vapor,
344 are premixed in a stainless-steel cylinder with high-purity gases purchased from Airgas
345 (H₂-99.9999%, He-99.9995%, N₂-99.9997%, CH₄-99.999%, CO₂-99.999%). The total
346 flow rate is 10 standard cubic centimeters per minute (sccm), and the premixed gas mixture
347 flows at a proportional rate of 10 sccm based on the mixing ratio. Water vapor is introduced
348 to the system at a pressure (corresponding to the mixing ratio) from HPLC water (Fisher
349 Chemical) at the desired temperature maintained by a dry ice/methanol/water cold bath. A
350 heating coil is employed to heat the gas mixture (including water vapor) to the experimental
351 temperature (400 or 300 K). The gas mixture is then exposed to an AC glow discharge in
352 a reaction chamber, which initiates complex chemical processes and leads to the formation
353 of new gas-phase products and solid particles. After 72 hours of continuous discharge flow,
354 we collect the haze analogues as powders and films on quartz substrate disks in a dry (<0.1
355 ppm H₂O), oxygen free (<0.1 ppm O₂), N₂ glove box (Inert Technology Inc., I-lab 2GB).
356 The haze analogues are kept in the glovebox until further analysis to avoid contamination
357 from Earth's atmosphere and light sources.

358 ***4.2 Density Measurements***

359 The density of exoplanet haze analogues has not been reported previously. We determine
360 the density of our haze analogues by measuring the mass and volume of a certain amount

361 of sample by using an analytical balance (± 0.0001 gram) and a gas pycnometer (AccPyc II
362 1340, Micrometrics), respectively. We first fill the powder sample to $\sim 70\%$ of a 0.1 cm^3
363 cup and measure the mass of the sample in the cup on the balance (where the mass of the
364 cup is known). Next, we measure the volume of the sample at ambient temperature with
365 the gas pycnometer that uses the gas (helium) displacement method to determine the
366 sample volume based on Boyle's law of volume–pressure relationships. We set the
367 pycnometer to measure 20 cycles, and the average volume from the 20 measurements is
368 reported with a standard deviation less than 0.0001 cm^3 . The density is then calculated by
369 dividing the mass by the volume.

370 ***4.3 Vacuum Fourier-transform Infrared Spectroscopy (FTIR) Measurement***

371 We employ a Vertex 70v FTIR spectrometer (Bruker Optics) to characterize the spectral
372 properties of the haze analogues. The Vertex 70v is a vacuum spectrometer, which can
373 eliminate the spectral features (H_2O or CO_2 absorption) from Earth's atmosphere and
374 increase the peak sensitivity without masking very weak spectral features. The wavelength
375 range of the spectrometer is 0.4 to $28.6 \text{ }\mu\text{m}$ ($25,000 \text{ cm}^{-1}$ to 350 cm^{-1}) with a maximum
376 resolution of 0.4 cm^{-1} , covering the whole observable wavelength range of *JWST* and a
377 large part of *Hubble*. This spectrometer is configured with a Reflection/Transmission
378 accessory (A510 Q/T, Bruker) and Seagull Variable Angle Reflection Accessory (Harrick
379 Scientific), allowing transmittance measurements and reflectance measurements at
380 different angles.

381 To derive the optical constants of the haze analogues, we measure the reflectance of the
382 film samples on quartz discs and transmittance of the powder samples using the potassium
383 bromide (KBr) pellet method. The films deposited on optical-grade quartz substrates in the
384 reaction chamber are directly used for the reflectance measurements (4.3.1). The procedure
385 for making KBr pellets is described in 4.3.2 and the transmittance measurements of the
386 pellets are described in 4.3.3.

387 **4.3.1 Reflectance Measurements of the films**

388 Using the Seagull Variable Angle Reflection Accessory, we measure the reflectance of
389 each haze analogue film at two different angles of incidence, 15° and 45°. The reflectance
390 of the films on quartz substrates is measured under vacuum (below 0.2 mbar) at room
391 temperature (294 K). We measure the reflectance in the wavelength range from 0.4 to 1.1
392 μm using a quartz beamsplitter and silicon diode detector. We acquire 1000 scans and
393 average them to obtain spectra with a resolution of ~5 cm⁻¹. The reflectance of an
394 aluminum standard mirror is measured as reference. The reflectance spectrum of the
395 sample is the ratio of the sample measurement to the reference measurement.

396 **4.3.2 Preparation of the KBr Pellets**

397 A quality KBr pellet is critical for quantitative measurements. To ensure that the pellet is
398 dry, KBr powder is dried in an oven overnight at 110 °C and immediately transferred to
399 the dry N₂ glove box after heating. Subsequent pellet-making steps are all performed in the
400 glove box. First, the KBr and the sample powders are separately ground to fine particles (<
401 2 μm) with ShakIR (a ball-mill grinder from Pike Technologies). Dry and fine KBr is used
402 to make a pure KBr pellet as a spectral reference. The fine particles of the sample and KBr
403 are mixed using the ShakIR to create a homogenous mixture of sample/KBr before making
404 pellets.

405 The concentration of the sample in KBr needs to be optimized for transmittance
406 measurements, usually between 0.5-3% depending on the absorption coefficients. Due to
407 the complex nature of the haze analogues, we prepare the haze/KBr mixtures with three
408 different concentrations to reveal both strong and weak absorption features in the samples.
409 The actual concentrations of our mixtures range from 0.08 to 4.1%. Because the quantities
410 of the haze analogues in the KBr pellet are relatively small, we use a two-step dilution
411 method to minimize errors in the measurement process. As reported in Myers et al. (2019)⁶⁰,
412 this method can reduce gravimetric error for the mass measurements from nearly 10% to

413 less than 1%. For example, to prepare a 0.1% mixture, we weigh 25 mg of the haze
414 analogue using the analytical balance (± 0.0001 gram) and mix it with 975 mg of KBr in
415 the ShakIR to create a 2.5% mixture; next, we take 40 mg of the 2.5% mixture and 960 mg
416 of pure KBr, and then mix them thoroughly using the ShakIR. After two dilutions, a 1:1000
417 (or 0.1%) homogenous sample/KBr mixture is ready to be pressed into a pellet.

418 Approximately 200 mg of finely ground KBr powder or homogenous mixture is placed
419 into a 13 mm pellet die (Pike Technologies), and then is pressed on a CrushIR 15 Ton
420 Digital Press (Pike Technologies). We apply 3 tons of force for 2 seconds, 7 tons for 30
421 seconds, and 10 tons for 120 seconds. The pressed pellet (diameter: 13 mm, thickness: ~ 0.5
422 mm) is removed from the die, mounted on a standard sample holder, and loaded into the
423 FTIR spectrometer for transmittance measurement.

424 **4.3.3 Transmittance Measurements of the Pellets**

425 We measure the transmittance of the pressed pellets over a wavelength range from 0.4 to
426 28.6 μm under vacuum (below 0.2 mbar) at room temperature (294 K). Two detectors
427 (silicon diode and DLaTGS detector) and two beamsplitters (quartz beamsplitter and KBr
428 beamsplitter) are used to cover the whole wavelength range. The silicon diode detector and
429 quartz beamsplitter are used from 0.4 to 1.11 μm (25000 to 9000 cm^{-1}); the DLaTGS
430 detector and quartz beamsplitter are used from 0.83 to 1.25 μm (12000 to 8000 cm^{-1}); and
431 the DLaTGS detector and KBr beamsplitter are used from 1.11 to 28.6 μm (9000 to 350
432 cm^{-1}). Overlapping data confirm that the spectrometer is calibrated properly across
433 different wavelength ranges. For each measurement, 500 scans are acquired with a
434 resolution of ~ 2 cm^{-1} . The transmittance of a pure KBr pellet is measured as a reference.
435 The transmittance spectrum of the sample is the ratio of the sample measurement to the
436 reference measurement.

437 **4.4 Optical Constants Derivation**

438 With the data from the measurements described above, we can derive the optical constants
 439 (complex refractive index, $n+ik$, where n is the real refractive index and k is the imaginary
 440 refractive index or the extinction coefficient) of the haze analogues. Based on the Beer-
 441 Lambert law, the absorbance (A) can be expressed as Equation 1 (Eq. 1):

$$442 \quad A = \alpha(\nu) * d \quad \text{Eq. 1}$$

443 where α is absorption coefficient, ν is the wavenumber, and d is the effective thickness of
 444 the sample. The absorbance (A) can be determined from the FTIR measurements (Eq. 2):

$$445 \quad A = -\ln T = -\ln \frac{I}{I_0} = \ln \frac{I_0}{I} \quad \text{Eq. 2}$$

446 where T is the transmittance, I is the light intensity passing through the sample (haze/KBr
 447 pellet), and I_0 is the light intensity of the reference (pure KBr pellet). The effective
 448 thickness (d) of the sample in the pellet is equal to:

$$449 \quad d = \frac{m}{\pi r^2 * \rho} \quad \text{Eq. 3}$$

450 in which m is the mass of the haze analogues in the pellet, r is the pellet radius (6.5 mm),
 451 and ρ is the measured density of the haze analogues.

452 Therefore, the absorption coefficient (α) can be calculated:

$$453 \quad \alpha(\nu) = \ln \frac{I_0}{I} / d \quad \text{Eq. 4}$$

454 Then, the extinction coefficient (k) can be determined:

$$455 \quad k(\nu) = \frac{\alpha(\nu)}{4\pi\nu} = \frac{1}{4\pi\nu d} \ln \frac{I_0}{I} \quad \text{Eq. 5}$$

456 For each sample, we obtain three sets of the extinction coefficients (k) independently by
 457 measuring the transmittance of three pellets with different effective thicknesses. The final
 458 k values are determined by averaging the three sets of k values.

459 With the determined extinction coefficient (k), we can calculate the real refractive index
 460 (n) based on the subtractive Kramers-Kronig (SKK) relation⁶¹⁻⁶³ between n and k as in Eq.
 461 6:

$$462 \quad n(\nu) = n_0 + \frac{2(\nu^2 - \nu_0^2)}{\pi} P \int_0^\infty \frac{\nu' k(\nu')}{(\nu'^2 - \nu^2)(\nu'^2 - \nu_0^2)} d\nu' \quad \text{Eq. 6}$$

463 where ν is wavenumber (cm^{-1}), n_0 is the real refraction index at ν_0 , and P indicates the
 464 Cauchy principal value. The principal P value is integrated for the entire wavelength range;
 465 we use the k values calculated (Eq. 5) from 350 to 25000 cm^{-1} in the integrand and assume
 466 constant k values for wavelengths beyond the measured range. The assumption is generally
 467 valid unless there are large local absorption peaks outside the measurement range. Using
 468 an anchor point (n_0) can reduce the uncertainty for the numerical integration as
 469 demonstrated in previous studies.^{62,63} However, the real refraction index of the haze
 470 analogues is initially unknown. From the interference fringes on the reflectance spectra of
 471 the film samples at two angles (15° and 45°) of incidence (see Extended Data Fig. 1), we
 472 determine n values from 0.4 to 1.1 μm using Eq. 7.

$$473 \quad n_0 = \sqrt{\frac{\sin^2\theta_1 * (\Delta\nu_1)^2 - \sin^2\theta_2 * (\Delta\nu_2)^2}{(\Delta\nu_1)^2 - (\Delta\nu_2)^2}} \quad \text{Eq. 7}$$

474 where θ_1 and θ_2 are the two different angles of incidence in our reflectance measurements
 475 of the film samples (15° and 45°), and $\Delta\nu_1$ and $\Delta\nu_2$ are the average fringe spacing in the
 476 reflectance spectrum at respective incidence angle (θ_1 and θ_2). The n_0 value determined at
 477 0.625 μm ($\nu_0=16000 \text{ cm}^{-1}$) is used as the anchor point for the numerical integration in Eq.
 478 6 to calculate the real refractive index (n) from 0.4 to 28.6 μm using the SKK relation. We
 479 used different anchor points (n_0 at different wavelengths) for the calculation and found that
 480 the yielded n values are very close (the difference is less than 2%).

481 *4.5 Atmospheric Transmission Spectra Simulation*

482 We use the open-source aerosol modeling code *Virga*⁴⁸ and the open-source radiative
 483 transfer suite *PICASO*⁴⁹ to compute haze Mie properties and implement them into a
 484 synthetic transmission spectrum model of an exoplanetary atmosphere. To generate hazy
 485 atmospheric model spectra, we require a stellar radius, planetary mass and radius, pressure-
 486 temperature profile, an atmospheric gas mixture, and haze profiles.

487 For the atmospheric composition of our synthetic spectra, we input the system parameters
 488 of GJ 1214 b for the stellar and planetary mass and radius⁴⁴ and the same gas mixing ratios
 489 as in the experimental run of the 400 K experiment shown in Fig. 1 into *PICASO*, using a

490 simple parametrized isothermal pressure-temperature profile at GJ 1214 b's T_{eq} of 600 K.
491 Into *Virga*, we input the optical properties of our experimental hazes as their real and
492 imaginary refractive indices n and k , binned down from the native measured resolution to
493 a spacing of 10 nm, which we verify is still a fine enough sampling to capture the spectral
494 features of the haze. We then used *Virga*'s optics functionality to generate wavelength-
495 dependent Mie coefficients using haze particle size distributions as measured in the
496 laboratory by He et al. 2018⁶⁴. In addition to the optical properties and particle size of the
497 experimental haze, we also need the vertical extent and mass loading of the haze layer
498 within *Virga* in order to compute a synthetic atmospheric transmission spectrum with
499 *PICASO*. *Virga* currently does not have the capability to self-consistently compute
500 photochemical haze profiles. Therefore, for simplicity, we implement an isobaric haze
501 layer from a pressure of 0.1 bar to 0.1 μ bar with haze mass loading of ~ 25 particle/cm³.
502 These values are consistent with the extent of haze in Titan's mesosphere⁶⁵ as well as self-
503 consistent haze formation modeling that has been performed for exoplanets.⁶⁶ The resulting
504 optical depth of the wavelength-dependent haze layers as a function of pressure and
505 wavelength from our model set-up is shown in Extended Data Fig. 2. For the Titan-like
506 haze cases, we use the same settings as described above for our 400 K and 300 K haze
507 layers, but substitute the refractive indices of Khare et al. (1984)¹⁴.
508 The purpose of our spectra simulation is to show the effect of the different haze optical
509 properties on the atmospheric transmission spectra rather than perform a full model
510 parameter study. Simplified assumptions were used in our simulation, such as atmospheric
511 pressure-temperature profiles, the particle radius and mass distribution. Future model
512 development and modeling studies, employing self-consistent pressure-temperature
513 profiles including the radiative effects of the haze¹⁷, and full microphysics treatment of
514 particle parameters⁶⁷⁻⁷¹, are required to fully explore haze impacts on observations of
515 exoplanet atmospheres.

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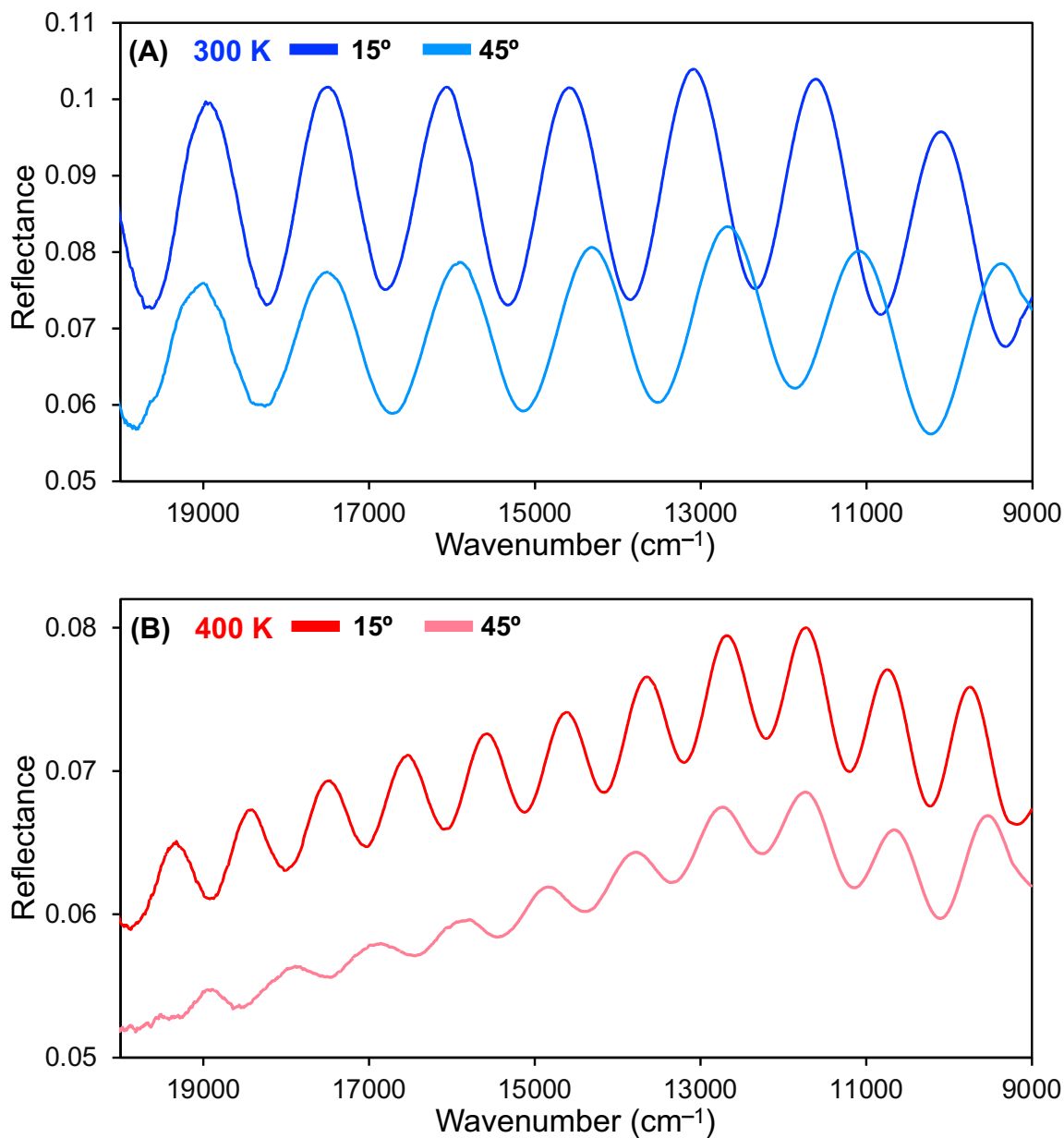
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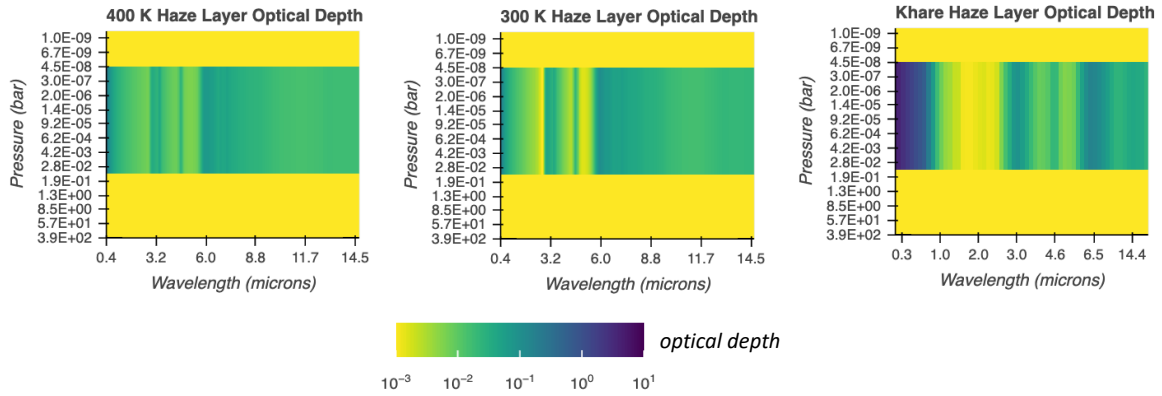
685 **Author contributions**

686 C.H., M.R., S.E.M., S.M.H., N.K.L., M.S.M., and J.I.M. conceived the study. J.I.M.
687 calculated the starting gas mixtures. C.H. carried out the experiments. C.H. and M.R.
688 performed the optical measurements. S.E.M. and C.H. simulated the synthetic transmission
689 spectra. C.H. conducted the data analysis and prepared the manuscript. All authors
690 participated in discussions regarding interpretation of the results and edited the manuscript.



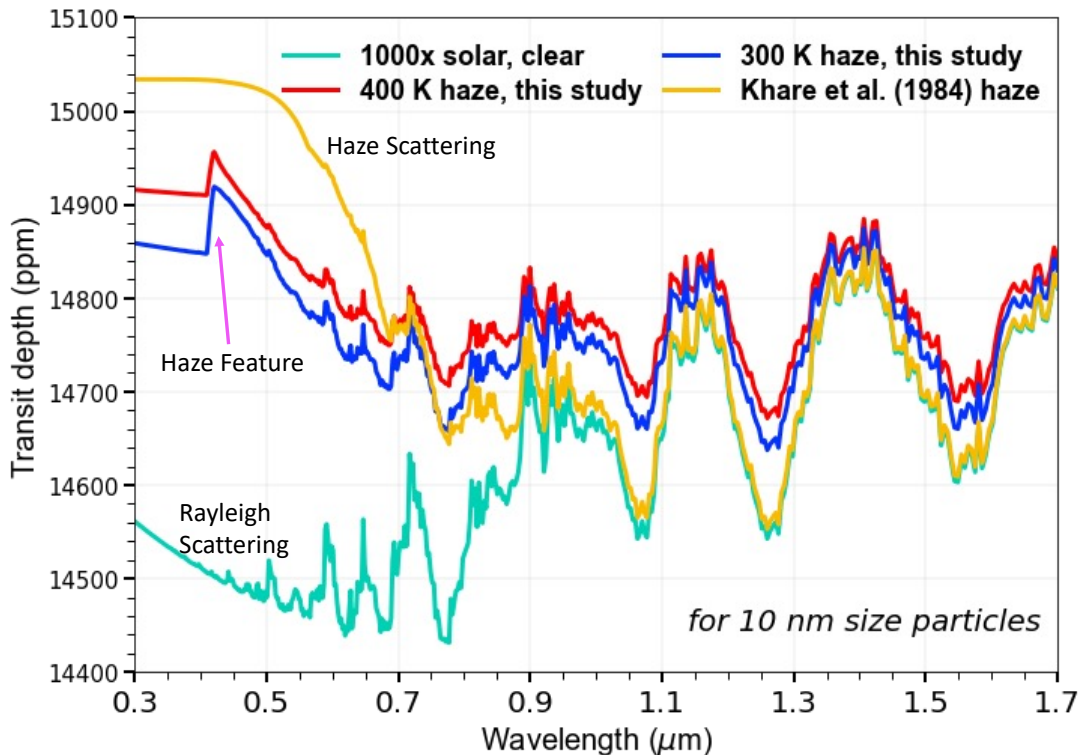
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692 **Extended Data Fig. 1.** Reflectance spectra of two exoplanet haze analogues formed in
 693 water-rich atmospheres at 300 K (A) and 400 K (B). Using Seagull Variable Angle
 694 Reflection Accessory, we measure the reflectance of each haze analogue film at two
 695 different angles of incidence, 15° (darker shade) and 45° (lighter shade). The spectra from
 696 20000 to 9000 cm⁻¹ (0.5 to 1.1 μm) are shown here. From the interference fringes on the
 697 reflectance spectra at two different angles, the n values of the samples at corresponding
 698 wavelengths can be determined using Eq. 7.



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Extended Data Fig. 2. Haze slab profiles as a function of pressure and wavelength as implemented with the *Virga*-derived Mie coefficients. The color bar indicates the optical depth at each wavelength, with darker shading corresponding to higher optical depths. The haze layer extends from 0.1 bar to 0.1 μ bar with a haze particle radii distribution centered around 25 nm. Note that the Khare et al. (1984) data has wider wavelength coverage than shown, but at lower resolution than our measured optical properties.



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Extended Data Fig. 3. Model spectra of a water-rich atmosphere around a GJ 1214 b -like planet. We show the effect of our newly measured haze optical properties using small radii (10 nm) haze particles, focusing on the wavelength range accessible to *Hubble*. The method

711 and settings for generating the spectra here are the same as described in 4.5, except the
712 haze particle radii (10 nm) and haze mass loading (4 particles/cm³). With sufficiently small
713 particles, the large scattering slopes between different haze compositions are differentiable
714 with *Hubble*'s ultraviolet/visible capabilities even if such hazes less strongly impact the
715 NIR.