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1 **Detection of hydrogen sulphide (H₂S) above the clouds in** 2 **Uranus' atmosphere**

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16 **The main cloud deck on Uranus is observed from visible to near-infrared observations to have**
17 **a cloud-top pressure of somewhere between 1.2 and 3 bar. However, its composition has never**
18 **been unambiguously identified, although it is widely assumed to be composed primarily of**
19 **either ammonia (NH₃) or hydrogen sulphide (H₂S) ice. Here we present evidence of a clear**
20 **detection of gaseous H₂S above this cloud deck in the wavelength region 1.57 – 1.59 μm**

21 **with a mole fraction of 0.4 – 0.8 ppm at the cloud tops. Its detection constrains the deep**
22 **bulk sulphur/nitrogen abundance to exceed 4.4 – 5.0 times the solar value in Uranus’ bulk**
23 **atmosphere, and places a lower limit on the mole fraction of H₂S below the observed cloud**
24 **of $(1.0 – 2.5) \times 10^{-5}$. The detection of gaseous H₂S at these pressure levels adds to the weight**
25 **of evidence that the principal constituent of 1.2 – 3-bar cloud is likely to be H₂S ice.**

26 In the absence of any spectrally identifiable ice absorption features, the identity of the main
27 component of the cloud in Uranus’ atmosphere with cloud top pressure 1.2 – 3 bar¹⁻³ has long
28 been a source of debate, although authors have most commonly ascribed it to be composed of
29 either ammonia (NH₃) or hydrogen sulphide (H₂S) ice³. This is based on the assumed presence
30 at deeper pressures (~ 40 bar) of an ammonium hydrosulphide (NH₄SH) cloud, which combines
31 together in equal parts any available H₂S and NH₃, leaving the remaining more abundant molecule
32 to condense alone at lower pressures⁴. Deeper in the atmosphere (20 – 40 bar), observations of
33 Uranus and Neptune at microwave wavelengths (1 – 20 cm) with the Very Large Array (VLA)⁵
34 found that there was a missing component of continuum absorption, which was concluded to be
35 likely due to the pressure-broadened wings of H₂S lines with wavelengths of less than a few mm.
36 The deep abundance of H₂S was estimated to be 10 – 30× solar and this analysis further concluded,
37 building upon previous studies^{6,7}, that the bulk S/N ratio must exceed ~ 5× the assumed solar
38 ratio⁸ in order that the bulk abundance of H₂S exceeds that of NH₃, leaving residual H₂S above
39 the deeper NH₄SH cloud. Hydrogen sulphide is believed to be a significant component of all
40 the giant planet atmospheres and has been detected *in situ* in Jupiter’s deep atmosphere by the
41 Galileo probe mass spectrometer⁹ (and also in comets, both *in situ* and remotely^{10,11}). However,

42 it has never been unambiguously remotely detected in the atmospheres of any of the giant planets,
43 aside from a possible debated detection in Jupiter’s atmosphere following the impact of Comet
44 Shoemaker-Levy 9 in 1994^{12,13}. Hence, while H₂S is probably the source of the missing continuum
45 absorption at microwave wavelengths in Uranus and Neptune’s atmospheres, and is also probably
46 the main component of the 1.2 – 3-bar cloud, it has never been unequivocally detected in Uranus’
47 atmosphere to confirm this.

48 Detection of H₂S and NH₃ absorption features at thermal-IR wavelengths is very challenging
49 due to the extremely cold atmospheric temperatures in Uranus’ atmosphere, but at visible/near-
50 infrared wavelengths, there are weak absorption bands that could potentially be detected in sun-
51 light reflected from the cloud tops at wavelengths where the absorption of other gases is weak.
52 The available line data for the key condensable volatiles in Uranus’ atmosphere (i.e. CH₄, NH₃,
53 H₂S) have recently been greatly improved and, although these absorptions are weak, we looked to
54 see whether we could detect these features in near-IR ground-based high resolution spectroscopic
55 measurements.

56 Observations of Uranus (with adaptive optics) were made with Gemini-North’s Near-infrared
57 Integral Field Spectrometer (NIFS) instrument in 2009/2010^{14,15}. NIFS records 3'' × 3'' image
58 ‘cubes’ with a pixel size of 0.103 × 0.043'', where each pixel is a spectrum covering, in the H-band,
59 the wavelength range 1.476 – 1.803 μm with a spectral resolution of R = 5290. For this study we
60 used observations recorded on 2nd November 2010 at approximately 06:00UT¹⁵. To minimise
61 random noise we averaged the observations over seven 5 × 5 pixel boxes, indicated in Fig. 1 and

62 listed in Table 1. We selected the wavelength region $1.49 - 1.64 \mu\text{m}$ for our analysis, comprising
63 $n_y = 937$ spectral points. We initially set the noise at each wavelength to be the variance of data
64 in these 5×5 pixel boxes. However, we found that we were not quite able to fit these spectra to
65 a precision of $\chi^2/n_y \sim 1$ and attributed this to unknown deficiencies in our spectral modelling.
66 We thus multiplied these errors by a single factor of 1.6 at all wavelengths (except for area ‘6’, for
67 which the variance was already sufficiently large) to account for these ‘forward-modelling’ errors.
68 For our reference spectrum we chose the region close to the disc centre, centred at 15.3°N (Area
69 ‘1’), but performed the same analysis for all other selected regions, reported in the supplementary
70 material.

71 To model the observed spectra we used the NEMESIS¹⁶ retrieval model, using the correlated-
72 k approximation with ‘k’-tables generated from the recently published WKLMC@80K+¹⁷ line
73 data for CH_4 and updated line data for H_2S and NH_3 from HITRAN2012¹⁸. The mean absorption
74 strengths of CH_4 , NH_3 and H_2S across the H-band wavelength range contained in these data (cal-
75 culated at 100 K and 1 atm) are shown in Fig. 1. Our *a priori* vertical atmospheric profile was
76 based on the ‘F1’ temperature profile, determined from HST/STIS and Voyager 2 observations³.
77 This profile has a deep methane mole fraction of 4%¹⁹, and has a varying relative humidity with
78 height above the condensation level. The He: H_2 ratio was set to 0.131 and the profile includes
79 0.04% mole fraction of Ne³. To this profile we added NH_3 and H_2S , assuming arbitrary ‘deep’
80 mole fractions (i.e. above the putative NH_4SH cloud) of 0.1% for both, and limited their abun-
81 dance to not exceed the saturated vapour pressure²⁰ in the troposphere as the temperature falls with
82 height, adjusting the abundance of hydrogen and helium (keeping He: H_2 = 0.131) to ensure the

83 mole fractions summed to unity at each pressure level. Figure 2 shows the modelled abundance
84 profiles of the three condensible species falling with height. We can see that the saturated vapour
85 pressure of H₂S at the pressure of the main clouds of Uranus (1.2 – 3 bar) is approximately 2000
86 times higher than that of NH₃. Hence, even though the peak NH₃ absorption strength in this spec-
87 tral region is, from Fig. 1, ~ 100 times stronger than that of H₂S, we expect the absorption lines
88 of H₂S to be far more visible due to the higher likely abundance of H₂S and also the lines of H₂S
89 having maximum strength at wavelengths of minimum methane opacity (Fig. 1). The very low
90 saturated vapour pressure of NH₃ at the 1.2–3 bar level in Uranus’ atmosphere makes it likely that
91 NH₃ would not have enough abundance to condense into a cloud with sufficient opacity at this
92 level as has previously been noted³.

93 We fitted the spectrum using a multiple-scattering model and modelled cloud opacity with
94 a vertically continuous profile of particles (at 39 levels) with a Gamma size distribution of mean
95 radius 1.0 μm and variance 0.05. This size distribution is typical of that assumed in previous
96 analyses^{2,21}, but is an assumption and is not constrained by, for example, a microphysical model.
97 In addition, the assumption that the particles have the same size distribution at all altitudes is
98 an oversimplification since we would expect that in real clouds the particles would be smaller at
99 higher altitudes. However, the primary objective of this study was to search for the spectral sig-
100 nature of H₂S gas, rather than to fit a sophisticated cloud model and we thus chose a model that
101 would be simple and easy to fit. It should be noted that our simple cloud model is used to model
102 not only the effects of the main 1.2 – 3 bar cloud, but also any CH₄ cloud opacity and any tropo-
103 spheric/stratospheric haze opacity that may be present. In addition to fitting the cloud opacity at

104 each level in the atmosphere, we also fitted the imaginary refractive index spectrum of the parti-
 105 cles (assumed to be the same at all vertical levels) at nine wavelengths between 1.4 and 1.8 μm ,
 106 reconstructing the real part of the refractive index spectrum using the Kramers-Kronig relation²¹,
 107 assuming $n_{real} = 1.4$ at 1.6 μm . We constrained the imaginary refractive index spectrum to vary
 108 reasonably slowly with wavelength, to avoid degeneracy with the H₂S signal we were trying to de-
 109 tect (see Methods). Self-consistent extinction cross-sections, single-scattering albedos and phase
 110 functions were then computed at all wavelengths using Mie theory, with the phase functions ap-
 111 proximated with Henyey-Greenstein functions (see Methods section). The total number of variable
 112 parameters in our retrieval was thus $n_x = 39 + 9 = 48$, and thus the total number of degrees of
 113 freedom, $n = n_y - n_x$ was 889.

114 Figure 3 shows our fit to the reference Uranus spectrum (Area ‘1’ of Fig. 1 and Table 1)
 115 when H₂S and NH₃ absorption is neglected, using three different *a priori* values of the imaginary
 116 refractive index of 0.001, 0.01 and 0.1, respectively, at all wavelengths with an *a priori* error
 117 of $\pm 50\%$. We can see that reasonably good fits are achieved for all three cases, but that better
 118 fits are achieved with higher *a priori* values, with similar results for $n_i = 0.01$ and $n_i = 0.1$
 119 ($\chi^2/n \sim 1.7$). For the $n_i = 0.001$ case, a poorer fit is achieved ($\chi^2/n \sim 1.9$) as the solution cannot
 120 move far enough away from the *a priori* to properly fit the spectrum. As a result the retrieved
 121 particles have low imaginary refractive index and so are more scattering, necessitating the cloud
 122 profile opacity to reduce quickly at pressures greater than 2–3 bar to prevent significant reflection
 123 from these levels. This is in stark contrast to the other two solutions, where n_i is much higher
 124 ($n_i \sim 0.06$), and where we find that the single-scattering albedo of the particles is $\varpi = 0.7–0.8$ and

125 phase function asymmetry is $g \sim 0.7$ across the observed spectral range (Supplementary Fig.1).
126 These retrieved single-scattering albedo and phase-function asymmetry values agree very well
127 with a limb-darkening analysis¹⁴, which used these same Gemini/NIFS data smoothed to a lower
128 resolution of FWHM = 0.004 μm and older, lower-resolution methane absorption k-distribution
129 data²², and also with an analysis of Keck and HST images²³, which recommended $\varpi = 0.75$ and
130 $g = 0.7$. An important consequence of the low single-scattering albedo of the retrieved particles is
131 that solar photons are quickly absorbed as they reach the cloud tops and so we do not see significant
132 reflection from particles residing at pressures greater than 2–3 bar. This can be seen in the retrieved
133 error bars for the cloud opacity profiles in Fig. 3 quickly relaxing back to their *a priori* value as
134 the pressure increases and the profiles for the higher n_i values tending smoothly back to their *a*
135 *priori* opacity/bar values. As a result, although we can clearly detect the cloud-top pressure at these
136 wavelengths, we cannot tell where the base is and thus cannot differentiate between a vertically
137 thin cloud based at 2–3 bar, or a cloud that extends vertically down to several bars with the same
138 cloud-top pressure. We also note here that when the particles are constrained to be more scattering,
139 the peak of cloud opacity is at a lower pressure than for the case with more absorbing particles.
140 This phenomenon may help to explain why HST/STIS³ retrievals, which assume the particles to
141 be more scattering, find the cloud tops to be at lower pressures (1.2 bar) than retrievals near 1.5
142 μm ^{1,2}, which assume more absorbing particles and find cloud tops at 2–3-bar.

143 Figure 4 compares our best fits to the observed reference spectrum (Area ‘1’ at 15.3°N) in
144 the 1.56 – 1.60 μm region, including or excluding H₂S absorption. When H₂S absorption is not in-
145 cluded, we find that there is a significant discrepancy between the measured and modelled spectra,

146 giving $\chi^2/n = 1.71$. This discrepancy is significantly reduced when H₂S absorption is included and
147 NEMESIS allowed to scale the abundance of H₂S, achieving a much closer fit with $\chi^2/n = 1.30$.
148 When H₂S absorption is not included, there are several peaks in the difference spectrum (Fig. 4)
149 that match perfectly the effect of including or excluding this gas in the spectral calculation. We ex-
150 amined the correlation between the expected H₂S signal and this difference spectrum between 1.57
151 and 1.60 μm , and found a Pearson correlation coefficient of 0.718 (indicating a strong correlation)
152 and a Spearman rank correlation coefficient of 0.602, with a two-sided significance value of $D =$
153 6.88×10^{-20} , which equates to a 9- σ -level detection. We also tested the effect on the calculated
154 spectrum of including or excluding 100% relative humidity of ammonia (NH₃), but found that this
155 was completely undetectable due to ammonia's extremely low abundances at these temperatures.
156 In case the ammonia abundance in Uranus' atmosphere is in reality highly supersaturated, we also
157 tested the effect on the calculated spectrum of supersaturating NH₃ by factor of 1000, also shown
158 in Fig. 4. However, we found that the absorption features of NH₃ do not coincide at all well with
159 the difference spectrum, with correlation coefficients of only 0.271 (Pearson) and 0.256 (Spear-
160 man), respectively. We thus conclude that NH₃ is not the source of the missing absorption. The
161 correlation between the spectral discrepancy of the fit, when H₂S is neglected, and the differences
162 between the modelled spectra when H₂S or NH₃ absorption is added are shown in Supplemental
163 Fig. 2.

164 The retrieved relative humidity of the H₂S profile needed to match the observed absorption
165 features was $113 \pm 12\%$. Since the mole fraction of H₂S decreases rapidly with height, this scaling
166 factor is strongly weighted by the abundance of H₂S just above the cloud tops, i.e. at 2–3 bar and

167 found to be 0.47 ppm, but is consistent with the H₂S profile having 100% relative humidity in this
168 region. However, this conclusion depends upon both the assumed temperature profile, which sets
169 the saturated vapour pressure, and also the assumed methane profile, which affects the retrieved
170 cloud-top pressure and thus the peak pressure level (and thus local temperature) of sensitivity
171 to H₂S. To test these effects we repeated our retrievals using a vertical profile of temperature
172 and abundance estimated from Spitzer²⁴, which has a lower CH₄ abundance of 3.2%, compared
173 with 4% for the ‘F1’ profile³, but is slightly warmer at pressures greater than 1 bar, resulting in
174 higher saturated vapour pressures of H₂S. As might be expected, the lower CH₄ abundance of this
175 profile led to the retrieved cloud opacity peaking at slightly higher pressures to achieve the required
176 column abundance of CH₄ (Table 1) and the retrieved H₂S relative humidity at the deeper cloud
177 tops in the warmer atmosphere was only $16 \pm 2\%$. Since it is not clear which of these two profiles is
178 more reliable, (although the ‘F1’ profile was found to be inconsistent with Spitzer observations²⁴) it
179 can be seen that although we clearly detect the presence of H₂S at Uranus’ cloud tops, it is difficult
180 to quantitatively determine its relative humidity. However, we can see from Table 1 that there is
181 very good correspondence between the retrieved values of column abundance of H₂S above the
182 clouds for the two temperature profiles and also between the retrieved mole fraction of H₂S at the
183 cloud-top pressure level of $(4.7 \pm 0.5) \times 10^{-7}$ for the ‘F1’ profile and $(4.3 \pm 0.5) \times 10^{-7}$ for the
184 Spitzer profile, where we have propagated the relative humidity retrieval errors.

185 Table 1 and Supplementary Figs. 3 – 11 show our fits at the other test points on Uranus’ disc,
186 indicated in Fig. 1. At all locations except in Uranus’ northern polar ‘cap’ feature we found a clear
187 improvement in our fit to the spectra when H₂S absorption is included, indicating the presence of

188 H₂S at the cloud tops (Table 1), with well defined column abundances of $(2 - 5) \times 10^{19}$ molecule
189 cm⁻² and cloud-top mole fractions of 0.4 – 0.8 ppm. All but one of the chosen points were on the
190 central meridian, to keep the zenith angle as low as possible to minimise the computation time of
191 our multiple scattering code, which uses more Fourier components in the azimuth decomposition
192 direction as the zenith angle increases to maintain accuracy. However, point ‘2’ was chosen to be
193 at roughly the same latitude as our reference area, but off the central meridian and closer to the
194 limb to check that our retrieval was robust against zenith angle changes, which was found to be
195 the case. The absence of a clear H₂S signature near Uranus’ north pole seems to indicate lower
196 H₂S above the clouds in this region, in the same way that microwave observations found that the
197 polar regions were depleted in microwave absorbers (H₂S and NH₃) at depth⁶. The abundance of
198 methane above the clouds is also known to be reduced at these latitudes^{3,19}. Alternatively, it could
199 also be that the H₂S signal is masked by increased abundance of tropospheric haze, but Table 1,
200 which lists a haze ‘index’, given by the observed radiance in a methane absorbing band divided
201 by the radiance at continuum wavelengths, does not suggest that the polar region is particularly
202 affected by overlying haze. However, to explore this further requires a detailed examination of
203 spectra in the polar regions, which is beyond the scope of this paper.

204 If we could be sure that the main observed cloud deck was vertically thin and composed of
205 H₂S ice, then we could constrain the abundance of H₂S below it by equating the cloud base to
206 the condensation level. However, the low retrieved single-scattering albedo of the cloud particles
207 means that we cannot tell between whether we are seeing a vertically thin cloud based at 2–3 bar
208 or just the top of a vertically extended cloud that extends to several bars. Instead, our detection of

209 H₂S can be used to give a lower limit on its abundance below the observed cloud. Assuming the
 210 main cloud is made of H₂S ice, is vertically thin and is based at 3 bars, and that the STIS/Voyager-
 211 2 ‘F1’ temperature profile³ we have assumed is correct, the saturated mole fraction of H₂S at the
 212 3-bar level (where the temperature is 116.1K) is estimated to be 1.1×10^{-5} . Alternatively, using
 213 the Spitzer profile²⁴, the saturated vapour mole fraction at the 3-bar level (where the temperature
 214 is 119.5 K) is 2.5×10^{-5} . Hence, we can conclude that the mole fraction of H₂S at pressures
 215 > 3 bar, immediately below the clouds must be $> (1.0 - 2.5) \times 10^{-5}$. We can compare this
 216 with the expected abundances of H₂S and NH₃ from microwave VLA studies⁵⁻⁷, who found the
 217 abundance of H₂S to be $10 - 30 \times$ solar, and $S/N > \sim 5$, assuming solar abundances⁸ of H₂S/H₂
 218 $= 3.76 \times 10^{-5}$ and NH₃/H₂ = 1.74×10^{-4} (giving N/S = 4.6). Using these values, $10 \times$ solar H₂S
 219 and $2 \times$ solar NH₃ would give a residual mole fraction of H₂S above a deeper NH₄SH cloud of at
 220 least 3×10^{-5} , while for $30 \times$ solar H₂S and $6 \times$ solar NH₃, the expected residual H₂S mole fraction
 221 increases to 9×10^{-5} . Both these values are significantly greater than our estimated minimum
 222 residual abundance, but are consistent with it and may suggest that the base of the cloud lies at
 223 pressures greater than 3 bar. A more recent analysis of Spitzer Uranus observations²⁴ suggests a
 224 residual H₂S mole fraction of 1.5×10^{-5} in order to reconcile the millimetre spectrum with the
 225 temperature profile derived from Spitzer, which is much closer to our estimate. Interpolating to
 226 the pressure levels in our assumed ‘F1’ temperature-pressure profile³ where the VLA and Spitzer
 227 estimates of residual H₂S abundance are equal to the saturated vapour pressure abundances we
 228 deduce that the base of the main cloud must lie at a pressure of 3.1 – 4.1 bar. Alternatively, if
 229 we assume the Spitzer temperature-pressure profile²⁴, we find a pressure range 2.8 – 3.7 bar. The

230 fact that we detect H₂S at all at Uranus' cloud tops confirms that the deep abundance of H₂S must
231 exceed that of NH₃ and hence that $S/N > 4.6 \times$ solar for the solar abundance ratios⁸ assumed
232 by the VLA study^{5,6}. We note, however, that there are other, more recent estimates of the solar
233 abundance ratios, for which the solar N/S value varies from 4.4²⁵ to 5.0²⁶. Hence, to ensure that
234 the deep abundance of H₂S exceeds that of NH₃ we conclude that the S/N ratio in Uranus' bulk
235 atmosphere exceeds 4.4–5.0 \times solar. The clear detection of gaseous H₂S above Uranus' clouds
236 leads us to conclude that H₂S ice likely forms a significant component of the main clouds at 1.2 – 3
237 bar. To our knowledge the imaginary refractive index spectrum of H₂S ice has not been measured
238 and hence we cannot directly verify if our retrieved refractive index spectrum is consistent with
239 H₂S ice. However, very large imaginary refractive indices, such as we retrieve, are absent in
240 the measured complex refractive index spectra of H₂O, CH₄ and NH₃ ices. This suggests that
241 if Uranus' main clouds are indeed formed primarily of H₂S ice, the particles may not be pure
242 condensates, but may be heavily coated or mixed with photochemical products drizzling down
243 from the stratosphere above, lowering their single-scattering albedos.

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330 data used. G.A.O. provided the Spitzer T-P profile used. L.N.F., N.A.T., D.T., and all co-authors contributed
331 to the analysis, interpretation of the results, and all co-wrote the final paper.

332 **Competing Interests** The authors declare that they have no competing financial interests.

333 **2 Figure Legends**

334 Figure 1. Panel A: The appearance of Uranus at $1.55 \mu\text{m}$, observed with Gemini/NIFS on 2nd
335 November 2010 at approximately 06:00UT, showing the position of the seven 5×5 pixel test areas
336 picked for retrieval analysis. Panel B: The appearance of Uranus at $1.62 \mu\text{m}$. Panel C: Reference
337 spectrum of Uranus¹⁴ analysed in this study, averaged over area ‘1’ just north of the equator, near
338 the disc centre, with a mean latitude of 15.3°N , and error estimates shown in grey. Panel D: Mean
339 strength listed in the k-distribution tables used in this study across the Gemini/NIFS spectral range.
340 These absorption tables were generated from the WKLMC@80K+¹⁷ database for CH_4 , and from
341 HITRAN2012¹⁸ for H_2S and NH_3 . These mean absorption coefficients have been computed at a
342 temperature of 100 K and pressure of 1 atm, similar to conditions found at the tops of Uranus’ main
343 visible clouds. Note that for NH_3 , the linedata in HITRAN2012 terminate at $1.587 \mu\text{m}$, roughly
344 half way through the H_2S absorption band.

345 Figure 2. Assumed pressure variation of temperature (left-hand panel) and condensible abun-

346 dance (right-hand panel) assumed in this study for Uranus. The temperature-pressure profile is
347 based on the ‘F1’ profile³. The vertical variation of the CH₄ abundance is as described in the text.
348 The abundances of NH₃ and H₂S have simply been limited by their saturation vapour pressures.

349 Figure 3. Fits to average Gemini/NIFS observation of Uranus, made on 2nd November 2010
350 at 15.3° N, using three different assumptions for the *a priori* imaginary refractive index spectrum,
351 and excluding H₂S and NH₃ absorption. The red line shows the results using $n_i = 0.001 \pm 0.0005$,
352 the black line shows the results using $n_i = 0.01 \pm 0.005$, while the blue lines show the results using
353 $n_i = 0.1 \pm 0.05$. Panel a) shows the fits to the measured spectra, panel b) shows the difference
354 between the observed and modelled spectra. Panel c) shows the fitted imaginary refractive index
355 spectra of the one type of particle assumed right hand plot, while panel d) shows the fitted cloud
356 profiles (opacity/bar at 1.6 μm). In panels c) and d) the *a priori* value and range is marked in light
357 grey, while the error range on the retrieved quantities is indicated in darker grey. The χ^2/n of the
358 fits is also shown in panel a).

359 Figure 4. Fits to the co-added Gemini/NIFS observation of Uranus in the wavelength range
360 1.56 – 1.6 μm . In the top plot, the observed reflectivity spectrum and estimated error is shown
361 in grey. The fitted spectrum when H₂S absorption is not included is shown in red, while the
362 fitted spectrum when H₂S absorption is included is shown in black. The bottom plot shows the
363 differences between these fits and the observed spectrum using the same colours (i.e. red when
364 H₂S absorption is not included and black when it is), with the error range again shown in grey. The
365 blue line in the bottom plot shows how the calculated spectrum for the fit when H₂S absorption is

366 not included (i.e. red line in the top plot) changes when H₂S absorption is added (leaving all other
367 fitted parameters unchanged), assuming a profile with 100% relative humidity (RH). The cyan line
368 shows how the calculated spectrum changes when NH₃ absorption is added, leaving all other fitted
369 parameters unchanged, assuming a profile with 1000 times the *a priori* NH₃ profile with 100%
370 RH.

371 **Methods**

372 **Spectral Data Sources** The main gaseous absorber in the H-band (1.4 – 1.8 μm) in Uranus' spec-
373 trum is methane. The best available source of methane line data at low temperature in this range is
374 the WKL_{MC@80K}+¹⁷ line database, which contains the positions, strengths, lower-state energies
375 and empirical estimates of the rotational quantum number J , of lines measured at 80K and 296K.
376 These lines are improved over the WK_{MC@80}²⁷ database, previously used to analyse the Gem-
377 ini/NIFS observations reanalysed here for Uranus² as they include extra lines that were detected at
378 296K, but not at 80K, and we have further improved our assignment of line widths, as described
379 below. For the lines detected at 296K, but not 80K, lower state energies were defined so as to yield
380 an intensity at 80 K just below the measurement sensitivity threshold. Hence, the contribution of
381 these lines at cold temperatures bears significant uncertainty. For the lines detected at 80K, but not
382 296 K, the lower state energies were arbitrarily set to -1.0 cm^{-1} . These line data were converted
383 to HITRAN format, using the listed strengths at 296 K directly for lines observed at both 80 K and
384 296 K, and for lines observed only at 80K, we extrapolated their strengths to 296 K using the listed
385 arbitrary lower state energy of -1.0 cm^{-1} and total partition function (rotational + vibrational)

386 provided as part of HITRAN2012¹⁸. The spectral range covered by these data is 5852 – 7919
387 cm^{-1} (1.262 – 1.709 μm). These measurements were made for “natural” methane gas, for which
388 the $\text{CH}_3\text{D}/\text{CH}_4$ ratio is estimated¹⁷ to be 5×10^{-4} . This is not suitable for calculations in Uranus’
389 atmosphere, for which the most precise estimate²⁸ of $\text{CH}_3\text{D}/\text{CH}_4$ is $(2.96_{-0.64}^{+0.71}) \times 10^{-4}$ (using an
390 isotopic enrichment factor²⁹ of $f = 1.68 \pm 0.23$). Hence, lines for CH_3D were scaled in strength
391 by 2.96/5. For the foreign-broadened line widths, we used J -dependent H_2 - and He-broadened
392 widths³⁰, to which we fitted a 4th-order polynomial in J , using the widths calculated for $J = 13$
393 for higher values of J to prevent inaccurate extrapolation^{31,32}. We assumed temperature depen-
394 dence coefficients of these foreign-broadened widths for H_2 -broadening³³ and He-broadening³⁵.
395 For the line shape, we used a Voigt function, but with sub-Lorentzian correction far from line cen-
396 tre as recommended for H_2 -broadening conditions³⁶. However, we also tested the sub-Lorentzian
397 corrections suggested for Titan spectra³⁷ and a sub-Lorentzian correction previously suggested for
398 modelling Uranus spectra³⁸. Using these three different line shapes we took account of all lines
399 within 250 cm^{-1} of each calculation wavelength.

400 Spectroscopic line data for hydrogen sulphide (H_2S) and ammonia (NH_3) were taken from
401 HITRAN2012¹⁸. The line widths and their temperature exponents were also taken from the foreign-
402 broadened data listed in HITRAN2012. For H_2S these are $\gamma_{air} = 0.074 \text{ cm}^{-1} \text{ atm}^{-1}$ and a tem-
403 perature exponent of 0.75, for all lines. HITRAN2012 note that detailed laboratory investigations
404 are needed to characterise how the line widths vary with the ro-vibrational quantum number, and
405 there appears to be no published evidence on the appropriate values for an H_2/He -broadening
406 atmosphere. Similarly, for NH_3 , we used the published HITRAN2012 foreign-broadening param-

407 eters. If the absorption of NH_3 had proved to be significant, we might have attempted to use line-
408 broadening parameters more suited to H_2/He -broadening conditions. However, as reported in our
409 paper, the absorption of NH_3 was not detected in these observations and hence there was no error
410 introduced by using the listed HITRAN2012 air-broadened widths. We also examined using Exo-
411 MOL line data for H_2S ³⁹ and found negligible differences in the spectra computed at Gemini/NIFS
412 resolution with the HITRAN2012 line data. Since the HITRAN2012 line data are much easier to
413 handle (they contain far fewer ‘hot lines’, which are only relevant for high-temperature calcula-
414 tions) and probably have better constrained line frequencies, we decided to use HITRAN2012 for
415 both NH_3 and H_2S line data. In both cases, in the absence of any better information and in the
416 expectation of weak absorptions (for which the exact line widths are less important), we used the
417 published HITRAN2012 air-broadened widths and a Voigt line shape, with a line wing cut-off of
418 35 cm^{-1} to account for typical sub-Lorentzian wing corrections.

419 The line data were converted to k-distribution look-up tables, or k-tables, covering the Gem-
420 ini/NIFS H-band spectral range, with 20 g-ordinates, 15 pressures, equally spaced in log pressure
421 between 10^{-4} and 10 bar, and 14 temperatures, equally spaced between 50 and 180 K. These tables
422 were precomputed with the modelled instrument line shape of the Gemini/NIFS observations, set
423 to be Gaussian with a full-width-half-maximum (FWHM) of $0.0003 \mu\text{m}$, after an analysis of ARC
424 lamp calibration spectra².

425 **Observations and wavelength calibration** Observations of Uranus were made with Gemini-
426 North’s Near-infrared Integral Field Spectrometer (NIFS) instrument in September 2009 and Octo-
427 ber/November 2010^{14,15}, with adaptive optics using Uranus’ nearby moons for wavefront sensing

428 (e.g. Ariel, Titania). NIFS’ H-band spectral resolution gives a Gaussian instrument function with
429 spectral resolution of $\text{FWHM} = 0.0003 \mu\text{m}$. The wavelength calibration provided by the standard
430 pipeline of Gemini/NIFS was found to be not quite accurate enough to match the spectral features
431 observed here. The assumed wavelength of sample i in the spectrum is set to $\lambda_i = \lambda_0 + (i - i_0)\lambda_1$
432 , where i_0 is the sample number of the ‘central’ wavelength, and the wavelength centre and step
433 were initially assumed to be $\lambda_0 = 1.55 \mu\text{m}$ and $\lambda_1 = 0.000155 \mu\text{m}$, respectively. By comparing
434 the measured spectrum to our initial fitted spectrum we found that we could achieve a much better
435 fit by modifying these values to $\lambda_0 = 1.54995 \mu\text{m}$ and $\lambda_1 = 0.00016036 \mu\text{m}$. We used these values
436 in the subsequent analysis.

437 **Uranus vertical profiles of temperature and gaseous abundance** The reference temperature
438 and abundance profile used in this study (Fig. 2) is based on the ‘F1’ STIS/Voyager-2 profile³.
439 This profile has a deep methane mole fraction of 4%¹⁹, and has a varying relative humidity with
440 height above the condensation level. The He:H₂ ratio in this profile is set to 0.131 and the profile
441 includes 0.04% mole fraction of Ne. To this profile we added abundance profiles of NH₃ and H₂S,
442 assuming arbitrary ‘deep’ mole fractions (i.e. above the putative NH₄SH cloud) of 0.001 for both,
443 and limited their abundance to not exceed the saturated vapour pressure in the troposphere as the
444 temperature falls with height. As the abundances of these gases (and CH₄) decrease with pressure
445 the abundance of H₂ and He is adjusted to ensure the sum of mole fractions adds to unity (keeping
446 He:H₂ = 0.131, or equivalently 12:88); the heights are calculated from the hydrostatic equation
447 using the local temperature, gravitational acceleration and local mean total molecular weight.

448 For comparison we also performed retrievals using the temperature-pressure profile deter-

449 mined by from Spitzer observations of Uranus' mid-IR spectrum²⁴, again with 'deep' NH₃ and
450 H₂S abundances of 0.001. H₂ and He were assumed to be present with a ratio 85:15, again ensur-
451 ing the sum of mole fractions adds to unity at all heights.

452 **Radiative-transfer analysis** The vertical cloud structure was retrieved from the Gemini/NIFS ob-
453 servations using the NEMESIS¹⁶ radiative-transfer and retrieval code. NEMESIS models planetary
454 spectra either using a line-by-line model, or by using the correlated-k approximation⁴⁰. For speed,
455 these retrievals were conducted using the method of correlated-k, but we regularly checked that
456 we obtained the same model spectra (to within error) using a line-by-line approach. To model
457 these reflected-sunlight spectra, a matrix-operator multiple-scattering model⁴¹ was used, with 5
458 zenith angles (upwards and downwards, respectively) and the number of required components in
459 the Fourier azimuth decomposition determined from the maximum of the reflected or incident-
460 solar zenith angles. The collision-induced absorption of H₂-H₂ and H₂-He was modelled with
461 published coefficients⁴²⁻⁴⁴. Rayleigh scattering was also included for completeness, but was found
462 to be negligible at these wavelengths.

463 To analyse the measured radiance spectra within our radiative transfer model we initially
464 used the high-resolution 'CAVIAR' solar spectrum⁴⁵, which we smoothed to the NIFS resolution of
465 $\Delta\lambda = 0.0003\mu\text{m}$. However, we found that this spectrum (and others, e.g.^{46,47}) contained spurious
466 'Fraunhofer lines' that did not seem to correspond to features seen at these wavelengths in the
467 Uranus spectra. We must assume that the method used to generate these 'Extraterrestrial Solar
468 Spectra' (ESS), namely measuring the solar spectrum at the ground at various zenith angles and
469 extrapolating to an airmass of zero, leads to small errors at these wavelengths. Hence, we used

470 a smoothed version of the solar spectrum⁴⁷ in our calculations, omitting the spurious ‘Fraunhofer
471 lines’, which we found matched our observations much more closely.

472 The observed spectrum (with $n_y = 937$ spectral points) was fitted with NEMESIS using a
473 continuous distribution of cloud particles whose opacity at 39 levels spaced between ~ 10 and
474 ~ 0.01 bar was retrieved. For this cloud profile the *a priori* opacity values (at $1.6 \mu\text{m}$) were set to
475 $0.001 \pm 0.0005 \text{ g}^{-1} \text{ cm}^2$ at all levels (equating to opacity/bar values of ~ 1), with a ‘correlation
476 length’ of 1.5 scale heights to ensure the profile was vertically smooth. NEMESIS treats cloud
477 opacity as log values and so the error was converted to $\pm 50\%$. The particles were assumed to
478 have a standard Gamma size distribution with mean radius $1.0 \mu\text{m}$ and variance 0.05, which are
479 typical values assumed in previous analyses. Using a previously published technique²¹, the imag-
480 inary refractive index of these particles was set to 1.4 at a wavelength of $1.6 \mu\text{m}$ and NEMESIS
481 used to retrieve the imaginary refractive index spectrum. The *a priori* imaginary refractive index
482 spectrum was sampled at every $0.05 \mu\text{m}$ between 1.4 and $1.8 \mu\text{m}$, with a ‘correlation length’ of
483 $0.1 \mu\text{m}$ set in the covariance matrix, to ensure that retrieved spectrum varied reasonably smoothly
484 with wavelength. Hence there were $n_x = 48$ free variables in our retrieval setup. At each iter-
485 ation of the model, the real part of the particles’ refractive index spectrum was computed using
486 the Kramers-Kronig relation⁴⁸. Self-consistent scattering properties were then calculated using
487 Mie theory, but the Mie-calculated phase functions were approximated with combined Henyey-
488 Greenstein functions at each wavelength to smooth-over features peculiar to perfectly spherical
489 scatterers such as the ‘rainbow’ and ‘glory’. This is justified since we expect the actual aerosols
490 in the atmosphere of Uranus to be solid condensates, and thus non-spherical. However, assuming

491 these non-spherical particles are randomly orientated with respect to each other, the bulk scattering
492 properties, such as cross-section and single-scattering albedo, are reasonably approximated with
493 Mie theory³⁴, especially if the phase functions are also modified as we describe.

494 Since methane is the main gaseous absorber we tested to see whether some of the approxi-
495 mations assumed in the WKLMC@80K+¹⁷ line database might be having an adverse effect on our
496 calculations. We first checked whether excluding the lines observed at 296 K, but not at 80 K (and
497 which are assigned a lower state energy high enough to reduce the computed strength at 80 K to
498 be below the measurement noise limit) might significantly affect the calculated spectra, but found
499 very little difference when these lines were neglected. We also checked the effect excluding the
500 lines observed only at 80 K as well (and which are assigned an arbitrary lower state energy of 1
501 cm^{-1}). In this case, the differences were larger, but on the whole the model correctly reproduced
502 the shape and main features of the observed spectrum.

503 **Retrieval Tests** Supplementary Fig. 12 shows our fit to the Uranus spectrum, setting the *a pri-*
504 *ori* imaginary refractive indices to 0.01 ± 0.005 at all wavelengths and using the three different
505 sub-Lorentzian line shapes for CH_4 (neglecting H_2S and NH_3 absorption). We found that each
506 assumption for the sub-Lorentzian correction gave a very similar fit to the spectrum ($\chi^2/n \sim$
507 1.7–1.9), which was initially puzzling. However, the reason for this is easy to understand from
508 Supplementary Fig. 12. The effect of different sub-Lorentzian corrections is most apparent on the
509 shortwave side of the strong absorption band at 1.7 – 1.8 μm and previous studies have tuned the
510 correction to get the best match to the observed spectrum between 1.5 and 1.62 μm . Our current
511 model, however, can very easily fit this region by varying the imaginary refractive index spectrum

512 of the particles and it can be seen that very different imaginary refractive index spectra are retrieved
513 for the three different sub-Lorentzian corrections, but very similar vertical cloud distributions and
514 similar spectral fits. In other words, there is a degeneracy between the sub-Lorentzian corrections
515 and the retrieved imaginary refractive index. In fact, we had to be careful not to allow the imagi-
516 nary refractive index retrieval too much freedom. Early retrievals sampled the imaginary refractive
517 index spectrum more finely ($\Delta\lambda = 0.005\mu\text{m}$) over the $1.56 - 1.6 \mu\text{m}$ range and significant part
518 of the spectral variation of reflectivity was accounted for by variations in n_i , which it was difficult
519 to justify as being realistic. We thus assumed the slow wavelength-to-wavelength variation in n_i
520 as described. Since the line shape recommended for H₂-He atmospheres³⁶ gave a good fit to the
521 observations, we chose to use this assumption in our final analysis.

522 **Scattering Properties** Since the fitted imaginary refractive index spectrum for our cloud particles
523 has values of typically $n_i \sim 0.06$, this leads the particles to be quite absorbing. This can best be
524 seen in Supplementary Fig. 1, where we compare the computed wavelength dependence of the
525 extinction cross-section (normalised to $1.6 \mu\text{m}$), the single-scattering albedo, and the asymmetry,
526 g , of the forward part of the fitted combined Henyey-Greenstein phase functions for the case when
527 the *a priori* imaginary refractive indices were set to 0.01 ± 0.005 . We found the back-scattering
528 part of the phase-function to be insignificant. As we can see the single-scattering albedo has values
529 of $\varpi = 0.7 - 0.8$, while the phase function asymmetry, g , is ~ 0.7 .

530 **3 Data availability statement**

531 The data that support the plots within this paper and other findings of this study are available from
532 the corresponding author upon reasonable request.

533 **4 Methods References**

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Table 1: Retrieval results at all areas considered on Uranus' disc.

Area	Latitude	p_1	f_{H_2S}	χ^2/n	χ^2/n_y	$\Delta\chi^2$	x_{H_2S}	A_{H_2S}	R_H
1 ^a	15.3°N	1.99	113 ± 12	1.30	1.23	367.3	0.47	2.7	2.1
2	13.8°N	2.00	134 ± 19	1.04	0.99	140.7	0.58	3.3	2.3
3	15.3°S	2.10	123 ± 16	1.23	1.17	225.1	0.80	4.9	2.5
4	32.5°N	1.88	303 ± 45	1.31	1.24	218.7	0.82	4.4	2.6
5	44.7°N	1.66	474 ± 84	1.33	1.26	172.9	0.43	2.1	2.8
6 ^b	62.0°N	1.56	252 ± 211	1.31	1.24	1.8	0.13	0.6	3.9
7	4.9°N	1.98	96 ± 9	1.57	1.48	333.8	0.38	2.2	2.2
1 ^c	15.3°N	2.28	16 ± 2	1.36	1.29	292.1	0.43	2.9	2.1

Notes: p_1 is the pressure(bar) where the cloud opacity to space is unity; f_{H_2S} is the retrieved H₂S relative humidity (%); χ^2/n is the reduced chi-squared statistic of the fit when H₂S is included, where $n = n_y - n_x = 889$; χ^2/n_y is the chi-squared statistic of the fit when H₂S is included, where $n_y = 937$; x_{H_2S} is mole fraction of H₂S (ppm) at p_1 ; A_{H_2S} is the column amount of H₂S (10^{19} molecule cm^{-2}) above p_1 ; R_H is a haze 'index' – the ratio of the average radiance from 1.63 – 1.64 μm divided by the average radiance from 1.57 – 1.58 μm , expressed as %.

Further notes: ^aArea 1 is the main area studied; ^bFor polar area 6, where the radiance is lower, the measurement errors did not need to be multiplied by 1.6 ensure a good χ^2/n ; ^cSame area as reference, but analysed using the Spitzer temperature profile, rather than 'F1'.

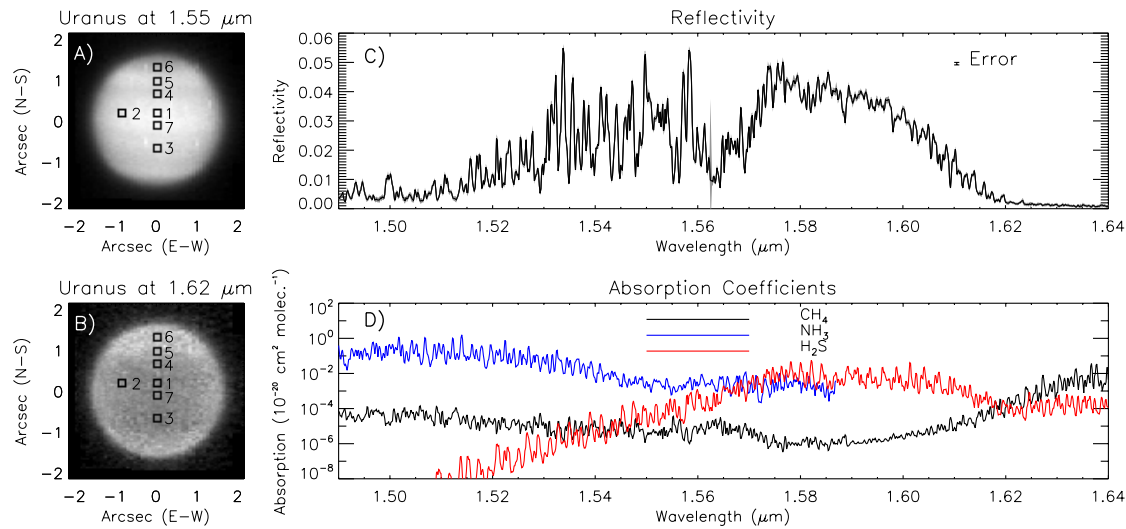


Figure 1: Panel A: The appearance of Uranus at 1.55 μm , observed with Gemini/NIFS on 2nd November 2010 at approximately 06:00UT, showing the position of the seven 5×5 pixel test areas picked for retrieval analysis. Panel B: The appearance of Uranus at 1.62 μm . Panel C: Reference spectrum of Uranus¹⁴ analysed in this study, averaged over area ‘1’ just north of the equator, near the disc centre, with a mean latitude of 15.3°N, and error estimates shown in grey. Panel D: Mean strength listed in the k-distribution tables used in this study across the Gemini/NIFS spectral range. These absorption tables were generated from the WKLMC@80K+¹⁷ database for CH₄, and from HITRAN2012¹⁸ for H₂S and NH₃. These mean absorption coefficients have been computed at a temperature of 100 K and pressure of 1 atm, similar to conditions found at the tops of Uranus’ main visible clouds. Note that for NH₃, the linedata in HITRAN2012 terminate at 1.587 μm , roughly half way through the H₂S absorption band.

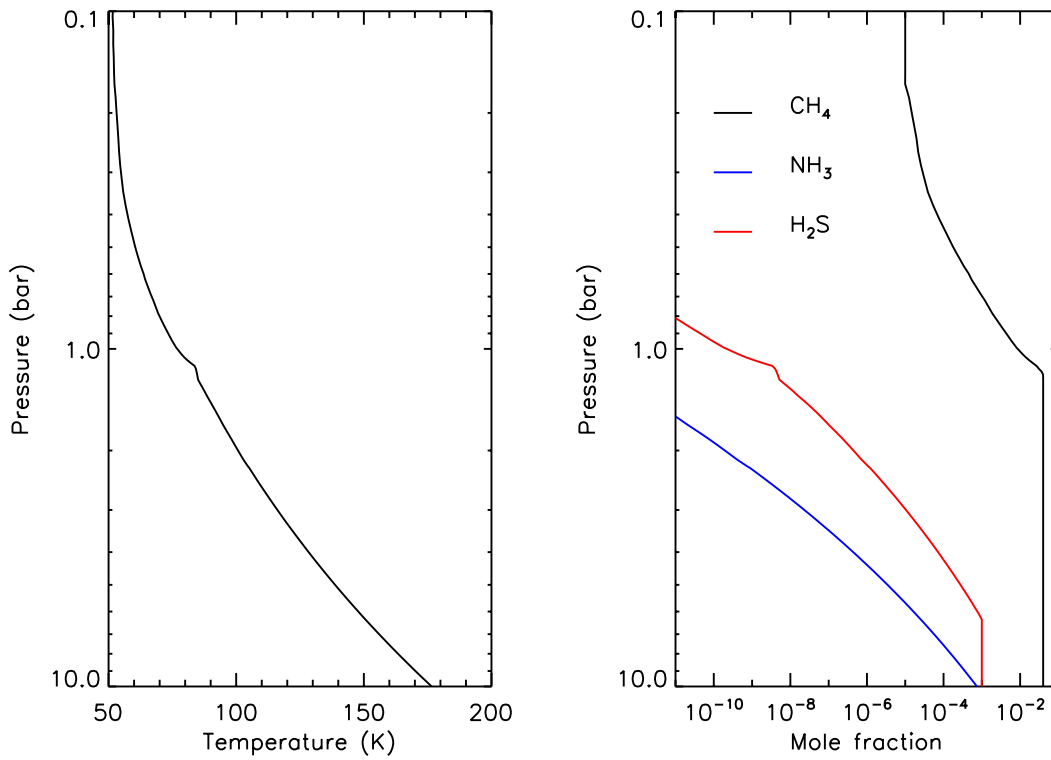


Figure 2: Assumed pressure variation of temperature (left-hand panel) and condensible abundance (right-hand panel) assumed in this study for Uranus. The temperature-pressure profile is based on the ‘F1’ profile³. The vertical variation of the CH_4 abundance is as described in the text. The abundances of NH_3 and H_2S have simply been limited by their saturation vapour pressures.

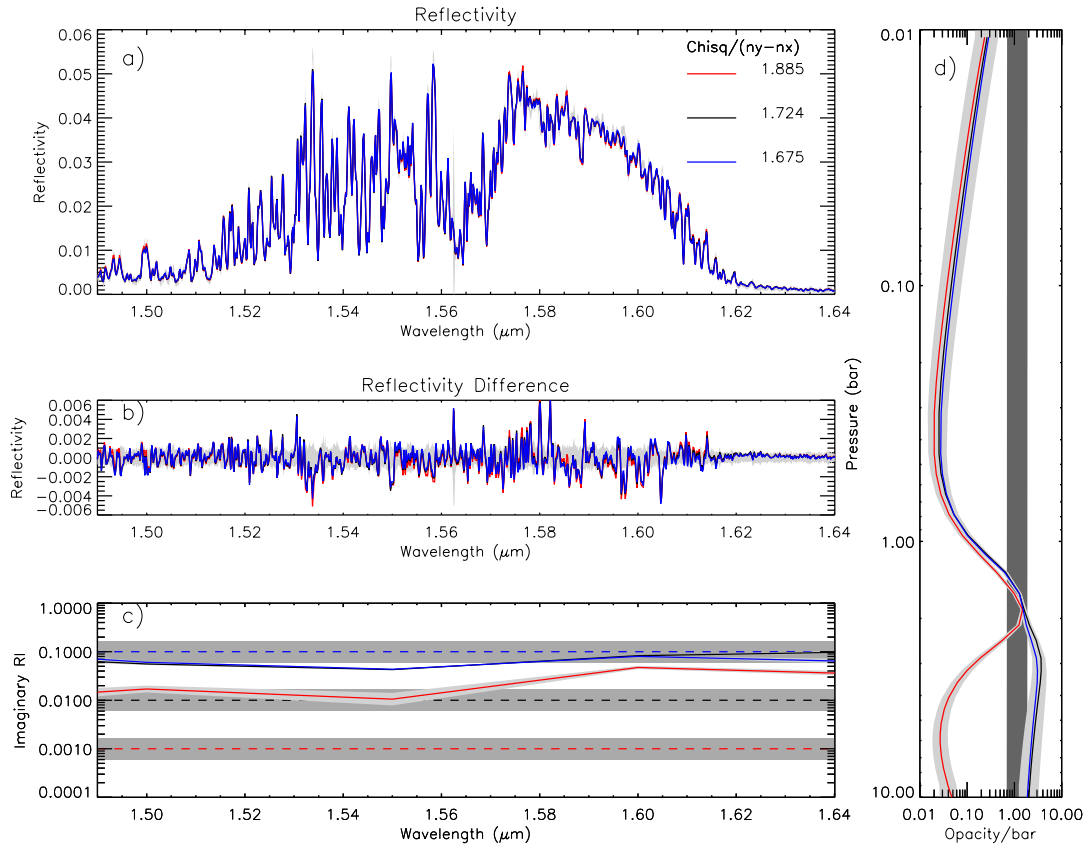


Figure 3: Fits to average Gemini/NIFS observation of Uranus, made on 2nd November 2010 at 15.3° N, using three different assumptions for the *a priori* imaginary refractive index spectrum, and excluding H_2S and NH_3 absorption. The red line shows the results using $n_i = 0.001 \pm 0.0005$, the black line shows the results using $n_i = 0.01 \pm 0.005$, while the blue lines show the results using $n_i = 0.1 \pm 0.05$. Panel a) shows the fits to the measured spectra, panel b) shows the difference between the observed and modelled spectra. Panel c) shows the fitted imaginary refractive index spectra of the one type of particle assumed right hand plot, while panel d) shows the fitted cloud profiles (opacity/bar at $1.6 \mu\text{m}$). In panels c) and d) the *a priori* value and range is marked in light grey, while the error range on the retrieved quantities is indicated in darker grey. The χ^2/n of the fits is also shown in panel a).

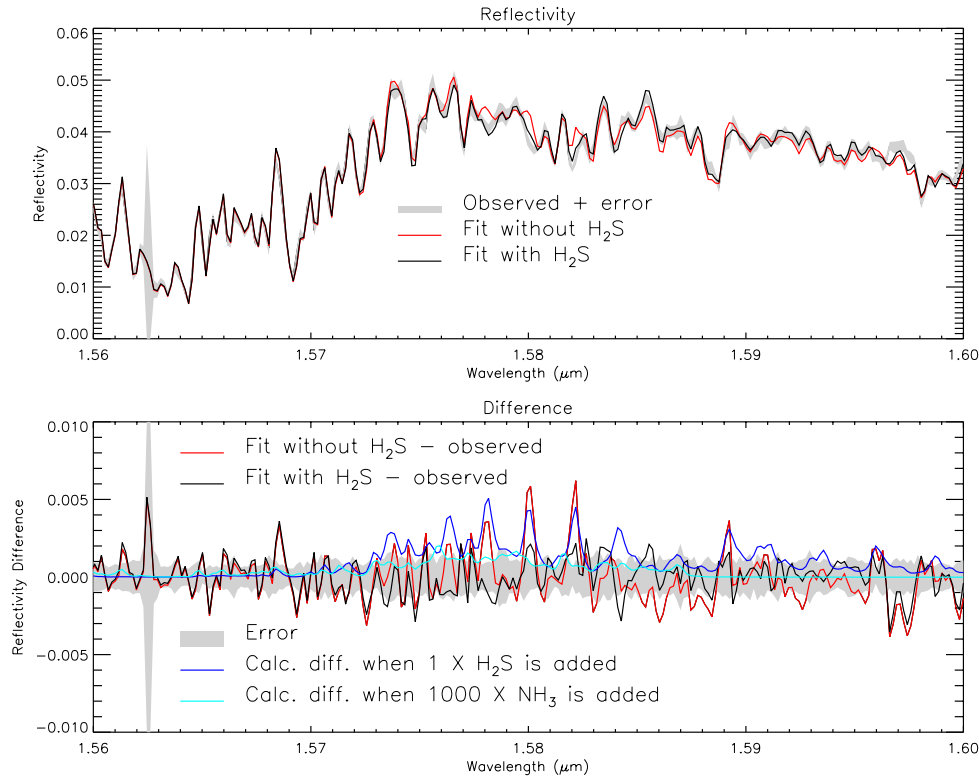


Figure 4: Fits to the co-added Gemini/NIFS observation of Uranus in the wavelength range 1.56 – 1.6 μm . In the top plot, the observed reflectivity spectrum and estimated error is shown in grey. The fitted spectrum when H_2S absorption is not included is shown in red, while the fitted spectrum when H_2S absorption is included is shown in black. The bottom plot shows the differences between these fits and the observed spectrum using the same colours (i.e. red when H_2S absorption is not included and black when it is), with the error range again shown in grey. The blue line in the bottom plot shows how the calculated spectrum for the fit when H_2S absorption is not included (i.e. red line in the top plot) changes when H_2S absorption is added (leaving all other fitted parameters unchanged), assuming a profile with 100% relative humidity (RH). The cyan line shows how the calculated spectrum changes when NH_3 absorption is added, leaving all other fitted parameters unchanged, assuming a profile with 1000 times the *a priori* NH_3 profile with 100% RH.