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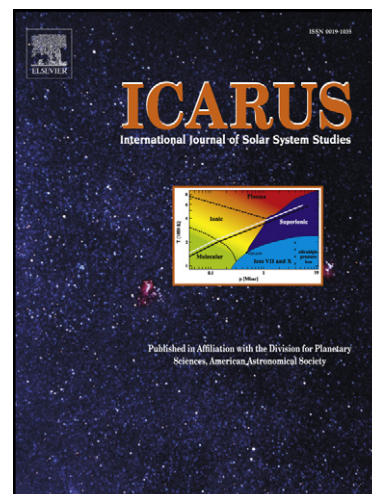
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Saturn's Tropospheric Composition and Clouds from Cassini/VIMS 4.6-5.1 μm Nightside Spectroscopy

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Abstract

The latitudinal variation of Saturn's tropospheric composition (NH_3 , PH_3 and AsH_3) and aerosol properties (cloud altitudes and opacities) are derived from Cassini/VIMS 4.6-5.1 μm thermal emission spectroscopy on the planet's nightside (April 22, 2006). The gaseous and aerosol distributions are used to trace atmospheric circulation and chemistry within and below Saturn's cloud decks (in the 1- to 4-bar region). Extensive testing of VIMS spectral models is used to assess and minimise the effects of degeneracies between retrieved variables and sensitivity to the choice of aerosol properties. Best fits indicate cloud opacity in two regimes: (a) a compact cloud deck centred in the 2.5-2.8 bar region, symmetric between the northern and southern hemispheres, with small-scale opacity

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variations responsible for numerous narrow light/dark axisymmetric lanes; and (b) a hemispherically asymmetric population of aerosols at pressures less than 1.4 bar (whose exact altitude and vertical structure is not constrained by nightside spectra) which is $1.5 - 2.0\times$ more opaque in the summer hemisphere than in the north and shows an equatorial maximum between $\pm 10^\circ$ (planetocentric).

Saturn's NH_3 spatial variability shows significant enhancement by vertical advection within $\pm 5^\circ$ of the equator and in axisymmetric bands at $23-25^\circ\text{S}$ and $42-47^\circ\text{N}$. The latter is consistent with extratropical upwelling in a dark band on the poleward side of the prograde jet at 41°N (planetocentric). PH_3 dominates the morphology of the VIMS spectrum, and high-altitude PH_3 at $p < 1.3$ bar has an equatorial maximum and a mid-latitude asymmetry (elevated in the summer hemisphere), whereas deep PH_3 is latitudinally-uniform with off-equatorial maxima near $\pm 10^\circ$. The spatial distribution of AsH_3 shows similar off-equatorial maxima at $\pm 7^\circ$ with a global abundance of 2-3 ppb. VIMS appears to be sensitive to both (i) an upper tropospheric circulation (sensed by NH_3 and upper-tropospheric PH_3 and hazes) and (ii) a lower tropospheric circulation (sensed by deep PH_3 , AsH_3 and the lower cloud deck).

Keywords: Saturn, Atmospheres, composition, Atmospheres, structure

1. Introduction

The Visual and Infrared Mapping Spectrometer (VIMS, Brown et al., 2004) onboard the Cassini spacecraft exploits a unique region of Saturn's spectrum between 4.6 and $5.1 \mu\text{m}$ where the effects of scattered sunlight diminish; the collision-induced opacity due to $\text{H}_2\text{-He}$ is at a minimum and strong CH_4 absorptions are absent. As a result, this wavelength range allows Cassini to probe deeper

7 into Saturn's troposphere than at any other infrared wavelength. As on Jupiter, this
8 $5\text{-}\mu\text{m}$ window is sensitive to the emission of the gas giant's internal heat, attenu-
9 ated by overlying cloud decks that appear in silhouette against the warm thermal
10 emission. To date, analysis of VIMS data has focussed on the detailed morphol-
11 ogy of images at discrete near-IR wavelengths (e.g., Baines et al., 2006; Baines
12 et al., 2009; Choi et al., 2009), which has revealed a wealth of information about
13 dynamical phenomena within Saturn's cloud decks (e.g., strings of pearls, ribbon
14 waves, the hexagon, polar vortices, annular clouds, and equatorial plumes; see the
15 review by Del Genio et al., 2009). However, the wavelength dependence of Sat-
16 urn's $4.6\text{-}5.1\ \mu\text{m}$ spectrum ($1950\text{-}2220\ \text{cm}^{-1}$) has yet to be fully exploited. In this
17 paper, we study the influences of gaseous distributions and cloud properties on
18 nightside VIMS spectra (i.e., sensitive to thermal emission alone, in the absence
19 of reflected sunlight) to determine the latitudinal distribution of opacity sources in
20 Saturn's troposphere.

21 Saturn's $5\text{-}\mu\text{m}$ window is expected to be similar to Jupiter's, albeit with a dif-
22 ferent vertical distribution of tropospheric aerosols due to Saturn's lower grav-
23 ity. Voyager/IRIS and Galileo/NIMS investigations demonstrated that Jupiter's
24 $5\text{-}\mu\text{m}$ emission was anticorrelated with both the visible albedo and with a vari-
25 able opacity cloud in the 1-2 bar region (e.g., Westphal et al., 1974; Terrile and
26 Westphal, 1977; Marten et al., 1981; Bevard et al., 1983; Irwin et al., 1998; Roos-
27 Serote et al., 1998; Irwin and Dyudina, 2002). This correlation is not readily
28 apparent on Saturn, where the visible belt/zone contrasts are subdued by the up-
29 per tropospheric hazes. Nevertheless, VIMS $5\text{-}\mu\text{m}$ images show extremely de-
30 tailed zonal organisation, with a diverse range of meteorological features (fine-
31 scale zonal lanes, small vortices and other turbulent structures), some of which

32 are common to both visible and 5- μm imaging (e.g., Choi et al., 2009; Vasavada
33 et al., 2006).

34 Orton et al. (2009) reviewed the first investigations of Saturn's 5- μm win-
35 dow from ground-based and space-based platforms, starting with the first spec-
36 troscopic detections of CH_3D (Fink and Larson, 1978) and phosphine (PH_3) by
37 Larson (1980) from the Kuiper Airborne Observatory. PH_3 was found to dominate
38 the shape of Saturn's 5- μm emission, but its poorly understood absorption coeffi-
39 cients hampered quantitative analyses of the 5- μm window for many years (Noll
40 and Larson, 1990). The abundance of PH_3 has since been studied at 5 μm using a
41 range of techniques (Bézard et al., 1989; Noll and Larson, 1990; de Graauw et al.,
42 1997). Ground-based observations began to reveal the other principal contributors
43 to the 5- μm spectrum: CO was first detected in UK Infrared Telescope measure-
44 ments (UKIRT) at 5 μm by Noll et al. (1986); germane (GeH_3) from UKIRT
45 (Noll et al., 1988) and later ISO de Graauw et al. (1997); and arsine (AsH_3) from
46 UKIRT (Noll et al., 1989) and the Canada-France-Hawaii Telescope (Bézard et al.,
47 1989). NH_3 bands ($2\nu_2$ and ν_4) affect the long-wavelength edge of this window
48 and were first detected by Fink et al. (1983), and later refined by Voyager/IRIS
49 (Courtin et al., 1984) and ISO (de Graauw et al., 1997). Detection of a subsolar
50 H_2O distribution at 5- μm had to wait for disc-averaged ISO spectra in the 1990s
51 (de Graauw et al., 1997). Finally, IRTF imaging at 5.1 μm indicated that Saturn's
52 deep cloud layers were spatially inhomogeneous (Yanamandra-Fisher et al., 2001)
53 before Cassini's arrival. Although the spectral resolution of VIMS is necessarily
54 smaller than ground-based instruments, it offers the capability to map the spatial
55 distribution of some of these gases for the first time, without having to correct for
56 telluric contamination.

57 Besides the wide ranging spectral effects of PH_3 , Saturn's poorly-understood
58 cloud properties further complicate quantitative analyses of the VIMS spectra.
59 The expected condensation altitudes for volatiles can be estimated using thermo-
60 chemical equilibrium theory and knowledge of bulk elemental abundances (Wei-
61 denschilling and Lewis, 1973; Atreya et al., 1999), although these do not account
62 for mixing via atmospheric motions. Assuming a five-fold enhancement in con-
63 centrations over solar composition, calculations by Atreya et al. (1999) suggested
64 that VIMS observations probe vertical dynamics and chemistry in the NH_3 (base
65 at 2 bar) and NH_4SH (base at 6 bar) ice cloud-forming regions of Saturn's tro-
66 posphere. Our present knowledge of Saturn's clouds, largely derived from visi-
67 ble and near-IR reflectivity studies, is reviewed by West et al. (2009). Common
68 features of the numerous studies (e.g., Karkoschka and Tomasko, 1992, 1993;
69 Stam et al., 2001; Temma et al., 2005; Pérez-Hoyos et al., 2005; Karkoschka and
70 Tomasko, 2005) include (a) a stratospheric haze ($1 < p < 90$ mbar) of small
71 radius ($r \approx 0.1 - 0.2\mu\text{m}$) particles, presumably originating from photochemical
72 processes; (b) a tropospheric haze from the tropopause down to the first conden-
73 sation cloud deck at 1.5-2.0 bar, possibly with aerosol-free gaps in the vertical
74 distribution; and (c) a possible thick NH_3 cloud, although no spectroscopic signa-
75 ture for NH_3 ice has been observed. As we shall demonstrate in Section 4, VIMS
76 is sensitive to a combination of these upper level ubiquitous hazes and the deeper
77 cloud decks.

78 The spatial distribution of NH_3 gas is intimately tied to the latitudinal vari-
79 ability of the hazes. Global constraints on the NH_3 vertical distribution have been
80 provided by a number of authors, as highlighted in Table 1. Generally, NH_3 was
81 found to be around 500 ppm below 3 bar (de Pater and Massie, 1985; Briggs

82 and Sackett, 1989), decreasing to 100 ppm at the condensation altitude (Briggs
83 and Sackett, 1989; Grossman et al., 1989; de Graauw et al., 1997; Orton et al.,
84 2000; Burgdorf et al., 2004) and then decreasing with altitude according to a sub-
85 saturated vapour pressure profile and photolysis in the upper troposphere (e.g., de
86 Graauw et al., 1997; Kerola et al., 1997; Kim et al., 2006; Fletcher et al., 2009b).
87 In this work we derive the latitudinal distribution of gaseous composition (NH_3 ,
88 PH_3 , AsH_3) and cloud opacity (tropospheric clouds and hazes) from VIMS obser-
89 vations of the $5\text{-}\mu\text{m}$ window. Section 2 describes the selection and error sources
90 in the VIMS data; Section 3 introduces the spectral model, techniques and opacity
91 sources allowing us to retrieve atmospheric properties. The degeneracies between
92 assumed cloud distributions and properties is explored in Section 4. Section 5
93 presents the VIMS-derived distributions of gases and clouds and Section 6 de-
94 scribes their implications for Saturn's tropospheric dynamics and chemistry.

95 **2. Observations**

96 *2.1. VIMS Data and Calibration*

97 Saturn's emitted radiance in the $4.6\text{-}5.1\ \mu\text{m}$ region is measured by the Visible
98 and Infrared Mapping Spectrometer (VIMS, Brown et al., 2004) on the Cassini
99 spacecraft. Although this instrument actually consists of two bore-sighted grating
100 spectrometers, only the infrared channel ($0.85\text{-}5.1\ \mu\text{m}$) is considered in the present
101 study. VIMS has a passively cooled linear array of 256 InSb photodiode detectors
102 operating at 55-60 K. VIMS-IR records spectral images by stepping a 2-axis scan
103 mirror orthogonally in the along-slit (64 pixel positions of the visible channel slit)
104 and cross-dispersion directions. One spectrum is acquired at each of 64 mirror
105 steps in the cross-dispersion direction, yielding an effective pixel size of 0.5 mrad

106 on a 64×64 pixel grid. The near-IR spectral resolution is approximately 15 nm,
107 sampled at intervals of 16.6 nm.

108 IR image cubes (two spatial and one spectral dimension) were geometrically
109 and photometrically calibrated (including despiking and flat-fielding with 2005
110 calibration files) by the VIMS Science team at the University of Arizona. The
111 VIMS calibration procedure was previously described by McCord et al. (2004),
112 although uncertainties in absolute calibration have not been fully documented
113 (Sromovsky and Fry, 2010b). Systematic errors from pre-flight calibration are
114 thought to be as large as 10% in regions of strong telluric H₂O absorption, al-
115 though random noise is expected to be considerably smaller (less than one digital
116 quantisation number, corresponding to approximately 0.1% of the typical 5- μ m
117 radiance). Radiometrically-calibrated VIMS-IR Images were navigated by re-
118 constructing ‘backplanes’ from the post-observation Cassini Mission SPICE ker-
119 nels generated by NASA/JPL (i.e., information on latitude and longitude, as well
120 as incidence, emission, azimuthal and phase angles) using the ISIS3 (Integrated
121 Software for Imaging Spectrometers) package provided by USGS (Gaddis et al.,
122 1997).

123 Artefacts in VIMS spectra identified by Sromovsky and Fry (2010b), partic-
124 ularly those associated with responsivity corrections near overlaps between order
125 sorting filters, are believed to have no effect on the 4.6-5.1 μ m spectrum (e.g.,
126 Fig. 8 of Brown et al., 2004). Light potentially scattered within the spectrometer
127 has also been identified as a source of enhanced reflectivity in low-signal regions
128 (Sromovsky and Fry, 2010b), although no such discrepancies between data and
129 models have been identified in the 5- μ m window. Finally, we found no evidence
130 for a shift in wavelengths from the nominal grid for any of the image cubes used in

131 this study. Nightside VIMS-IR radiances were assigned uncertainties by consider-
132 ing the larger of (i) 12% of the radiance measured by each pixel, or (ii) 12% of the
133 mean radiance in the 4.6-5.1 μm range. This avoided unequal weightings of re-
134 trievals to the low-signal regions of the Saturn spectrum (see Section 3). The 12%
135 envelope is conservative, adding quadrature-estimated errors due to pre-flight cal-
136 ibration as well as forward-model uncertainties on spectral line data. Specifically,
137 we assumed that systematic errors dominate the error budget.

138 2.2. Data Selection

139 Reflected sunlight observations of the giant planets are complicated by the un-
140 certain optical properties (shape, size distribution, composition, phase function,
141 opacity) of their cloud and haze layers. To minimise these effects, we considered
142 only VIMS nightside spectra at a sufficient distance from the day/night termina-
143 tor to ignore scattered sunlight. Scattered sunlight from Saturn's rings is unlikely
144 to contaminate the nightside Saturn spectra, as water ice in the rings has a low
145 albedo at all VIMS wavelengths beyond 2.8 μm , and is particularly dark near 3
146 and 5 μm (Cuzzi et al., 2009). Thermal emission from the atmosphere, in addi-
147 tion to absorption and scattering processes, should determine the overall shape of
148 the 4.6-5.1 μm spectrum. This study uses eight VIMS-IR image cubes from se-
149 quence VIMS_023SA_MIRMAPB010 (part of sequence S20) on April 22, 2006
150 (Table 2). Saturn subtended 3.1° during these observations, at a distance of 2.2
151 million km (38 Saturn radii). The relatively large spacecraft range meant that al-
152 most the entirety of Saturn was captured within the 32×32 mrad field of view,
153 allowing multiple latitudes to be covered in a single cube (from 40°S to 70°N).
154 Saturn's sub-solar latitude was 17.6°S during these observations (a heliocentric
155 longitude, $L_S = 317.3^\circ$) approaching the southern autumnal equinox. As such,

156 seasonal hemispheric asymmetries in cloud coloration and atmospheric tempera-
157 tures (Fletcher et al., 2010) were still present.

158 The eight VIMS cubes sampled Saturn during an entire 10-hour rotation (Table
159 2) so that a composite image from these cubes covered 360° of longitude (Fig. 1).
160 The longitudinal displacement of individual features over the 10-hour sequence
161 was not accounted for in the rejections, and this is particularly apparent in the
162 overlap region of the first and last cubes in Table 2 (120°W). Four wavelengths
163 (4.6 to $5.1 \mu\text{m}$) are displayed to demonstrate that atmospheric features appear
164 similar across the spectral range, and that an asymmetry between the northern and
165 southern mid-latitudes persisted in April 2006 (Baines et al., 2006). Indeed, the
166 map at $4.6 \mu\text{m}$ (Fig. 1d) shows a well-defined boundary at 10°N between the bright
167 north and dark south, and that the equatorial zone is largely indistinguishable from
168 the rest of the southern hemisphere at this wavelength.

169 The dark equatorial zone is bordered by two regions of diffuse emission be-
170 tween $\pm 5^\circ$. This axisymmetric band is colocated with the narrow prograde jet
171 identified by García-Melendo et al. (2010), which exists in addition to the broad
172 equatorial jet. An irregular chain of dark features (referred to as equatorial plumes)
173 impinge on these diffuse regions from both north and south. Mid-latitudes be-
174 tween $\pm 5 - \pm 32^\circ$ show the strongest asymmetry between the hemispheres, with
175 the northern hemisphere considerably brighter than the south. Both hemispheres
176 are characterised by a series of latitudinally-narrow bright and dark lanes, similar
177 to those observed in reflected sunlight (Vasavada et al., 2006; Choi et al., 2009).
178 Some discrete features are observed at off-equatorial latitudes (particularly in the
179 bands between $20-30^\circ$ in both hemispheres), although the spatial resolution of the
180 S20 sequence of images is insufficient to characterise small-scale features such as

181 the String of Pearls at 33°N (Momary et al., 2006; Choi et al., 2009).

182 Zonal mean radiances were extracted from the reprojected maps onto two dif-
183 ferent meridional grids: (i) a coarse grid with a step size and latitude width of
184 5° for preliminary testing; and (ii) a fine grid with a size and width of 1° for the
185 final zonal profiles. Within each latitude bin, we selected spectra within 10° of the
186 minimum emission angle for the latitude, and restricted selections to phase angles
187 greater than 90° and solar angles greater than 120° - i.e., ensuring that only night-
188 side observations contributed to the average. The hemispheric asymmetry can be
189 clearly seen in the spectral comparison in Fig. 2. Radiances and brightness tem-
190 peratures for the 4.6-5.1 μm region are compared for five latitudes, showing that
191 the northern mid-latitudes were uniformly 10-12 K brighter than southern mid-
192 latitudes in April 2006. The overall morphology of the spectrum is dominated by
193 absorption from PH_3 gas and tropospheric aerosols, although the band centres for
194 a variety of gases are labelled in Fig. 2b. Note that the broad absorption feature at
195 4.74 μm is a blend of absorptions due to PH_3 , GeH_4 , AsH_3 and CO . The unusual
196 ‘kink’ in the equatorial spectrum at 5.1 μm that is absent from other latitudes is a
197 signature of tropospheric NH_3 .

198 3. Spectral Modelling

199 Fig. 2 showed that VIMS-IR spectra in the 4.6-5.1 μm range are sensitive to a
200 wide variety of gases and aerosols, but that the spectral resolution (approximately
201 15 nm, or $R = \lambda/\Delta\lambda \approx 330$ at 5 μm) is insufficient to resolve the individual lines.
202 Instead, they blend together into absorption complexes, requiring simultaneous
203 modelling of the entire range to derive the best-fitting atmospheric profile at each
204 latitude. In this section we describe the basic spectral model before exploring the

205 degeneracies associated with the VIMS spectra in Section 4.

206 3.1. Reference Atmosphere

207 Saturn's *a priori* atmospheric structure (temperatures, $T(p)$, and mole frac-
208 tions, $q(p)$) was defined on a grid of 39 levels equally spaced in $\log p$ between 10
209 mbar and 10 bar. Temperatures at each latitude were obtained from Cassini/CIRS
210 $T(p)$ profiles from Cassini's prime mission (sensitive to the 1-800 mbar range,
211 Fletcher et al., 2010), and extrapolated between 0.8 and 10 bar with a dry adiabatic
212 lapse rate, g/c_p (where g is the latitudinally-variable gravitational acceleration at
213 1 bar and c_p is the specific heat capacity of Saturn's H_2 -He- CH_4 atmosphere).

214 Collision-induced absorption of H_2 - H_2 , H_2 -He, H_2 - CH_4 and CH_4 - CH_4 was
215 pre-calculated from the tabulations of Borysow (1991, 1993); Borysow et al. (1988);
216 Borysow and Frommhold (1986, 1987) and references therein. The helium mix-
217 ing ratio He/H_2 was set to 0.135 (Conrath and Gautier, 2000). Methane and its
218 isotopologues are well-mixed throughout the altitude range of interest, and were
219 included with mole fractions of 4.7×10^{-3} (CH_4); 3.0×10^{-7} (CH_3D) and 5.1×10^{-5}
220 ($^{13}\text{CH}_4$) following Fletcher et al. (2009b). The PH_3 profile was set to the CIRS-
221 derived abundance of 6.4 ppm at $p > 0.55$ bar, decreasing due to photolysis at
222 lower pressures with a fractional scale height of 0.27 (the ratio of the PH_3 scale
223 height to the scale height of the bulk atmosphere, Fletcher et al., 2009a). The verti-
224 cal distribution of NH_3 had a deep mole fraction of 60 ppm (Fletcher et al., 2009b),
225 decreasing with altitude following a saturated vapour pressure profile ($p > 0.3$
226 bar) and a linear extrapolation to low pressures to represent photolysis ($p < 0.3$
227 bar). Minor constituents affecting the 4.6-5.1 μm range were assumed to be well-
228 mixed with altitude, and were included with the following mole fractions: CO (1
229 ppb, Noll and Larson, 1990); GeH_4 (0.4 ppb, Noll and Larson, 1990); AsH_3 (3.0

230 ppb, Noll and Larson, 1990); and H₂O (well-mixed at 0.176 ppm over the altitude
231 range of interest, de Graauw et al., 1997).

232 3.2. Sources of Line data

233 The near-infrared spectral line database was updated from that used by Ir-
234 win et al. (1998); Roos-Serote et al. (1998) for Galileo/NIMS analysis, who pre-
235 dominantly used line data extracted from GEISA 1992 (Husson et al., 1992).
236 HITRAN2004 (Rothman et al., 2005) was used for CO, H₂O, CH₄, CH₃D and
237 ¹³CH₄. Absorption due to phosphine's pentad polyad dominates the VIMS 5- μ m
238 spectrum, with the $2\nu_2$ band at 5.07 μ m and the broad $\nu_2 + \nu_4$ band between 4.69
239 and 4.78 μ m. Furthermore, the ν_1 and ν_3 bands absorb shortward of 4.58 μ m
240 and contribute to the reduced thermal emission at these wavelengths. GEISA2003
241 (Jacquinet-Husson et al., 2005) was used for PH₃ as it contained updates from
242 Kleiner et al. (2003) for some missing bands in the 5- μ m window. However, the
243 PH₃ absorption coefficients are still subject to considerable uncertainty, as the
244 original intensity studies of Tarrago et al. (1992) are estimated to have only a
245 20-30% accuracy. Work is underway to compare this band to the dyad at 9 μ m
246 (Fusina and Di Lonardo, 2000; Brown et al., 2002) and the octad at 2.9 μ m (Butler
247 et al., 2006). GEISA2003 was also used for GeH₄, and contained updated 0-5300
248 cm⁻¹ line data for NH₃ from Kleiner et al. (2003). AsH₃ was not present in ei-
249 ther database, so we used line data from Dana et al. (1993) and Mandin (1995),
250 following the NIMS analyses of Irwin et al. (1998); Roos-Serote et al. (1998).

251 Foreign broadening (by H₂) for each of the molecules was estimated for all
252 lines as follows. GeH₄ was broadened with a half-width of 0.1 cm⁻¹ atm⁻¹ and
253 a temperature dependence $T^{0.75}$ (Jacquinet-Husson et al., 2005). AsH₃ had a half
254 width of 0.075 cm⁻¹ atm⁻¹ and $T^{0.5}$ (an assumption based on PH₃). PH₃ used es-

255 timated half-widths from Kleiner et al. (2003) and $T^{0.65}$. NH_3 had a half-width of
256 $0.072 \text{ cm}^{-1} \text{ atm}^{-1}$ and $T^{0.73}$ (B. Bézard & L. Brown, *pers comms.*). The spectro-
257 scopic data for each gas were used to generate k -distributions (ranking absorption
258 coefficients, k , according to their frequency distribution, Irwin et al., 2008) using
259 a 16 nm FWHM on an evenly sampled wavelength grid of 8 nm spacing. We use
260 a direct sorting method to calculate the k -distribution from line-by-line spectra
261 within each spectral bin (e.g., Goody et al., 1989). A triangular instrument func-
262 tion was used for spectral modelling, which was found to be a good approximation
263 for grating spectrometers with rectangular entrance slits and linear arrays of detec-
264 tors, and allows rapid convolution over the k -distribution. The use of pre-tabulated
265 k -distributions greatly accelerates spectral calculations and permits rapid retrieval
266 of atmospheric spectra.

267 3.3. Forward Modelling and Retrieval

268 VIMS spectra were analysed using a suite of radiative transfer and retrieval
269 codes developed at the University of Oxford (Nemesis, Irwin et al., 1997; Ir-
270 win et al., 2008), which have been previously used to investigate Galileo/NIMS
271 near-IR spectra of Jupiter (e.g., Irwin et al., 1998; Irwin and Dyudina, 2002) and
272 Cassini/CIRS thermal-IR spectra of Jupiter and Saturn (e.g., Fletcher et al., 2009a,
273 2010). The correlated- k method (Goody et al., 1989; Lacis and Oinas, 1991)
274 is used for rapid calculation of non-monochromatic transmission along an inho-
275 mogeneous atmospheric path based upon pre-tabulated absorption coefficients,
276 aerosol extinction cross-sections and collision-induced absorption. Retrievals of
277 temperature, aerosol and gaseous composition are achieved using optimal estima-
278 tion (Rodgers, 2000), but adapted for planetary applications by tuning *a priori*
279 uncertainties to achieve the optimal trade-off between precision (the quality of the

280 spectral fit to the data) and physically-realistic solutions (Irwin et al., 2008). Re-
281 trievals require calculations of both the upwelling radiance, $I(\lambda)$, as well as the rate
282 of change of radiance with the model parameters (dI/dx), based on the reference
283 atmosphere (Section 3.1), which is perturbed in successive iterations (based on a
284 Marquardt-Levenburg braking parameter, Press et al., 1992) to converge on the
285 optimal solution. The algorithm seeks to minimise the residual between measured
286 and modelled spectra (the traditional χ^2).

287 The 5- μm window can be modelled assuming thermal emission from the planet,
288 attenuated by absorbing clouds. We neglect any thermal emission from the clouds
289 themselves, as these reside at higher, cooler (by 50-80 K) altitudes than the source
290 of the upwelling radiance (the 4-6 bar region, where temperatures reach approx-
291 imately 240 K, see Section 3.5). In this case the functional derivatives (or Ja-
292 cobians, dI/dx) are computed analytically, permitting rapid convergence to the
293 optimal solution. However, multiple scattering from aerosols in the real Saturnian
294 atmosphere will increase the optical paths of individual photons, thereby enhanc-
295 ing the gas absorptions and decreasing the molecular abundances required to re-
296 produce the spectra.

297 The Nemesis software performs full multiple-scattering calculations (either
298 for thermal emission, reflected sunlight or a combination of both) using a matrix
299 operator (or doubling-adding) approach (Plass et al., 1973; Hansen and Travis,
300 1974) in a plane-parallel atmosphere, but numerical-differencing must be used to
301 evaluate the functional derivatives due to the complexity of the multiple-scattering
302 scheme. Integration of the scattered radiance over all solid angles was simplified
303 in two ways: first, the integration over zenith angle used a Lobatto quadrature
304 scheme with five angles to reduce the calculation to a simple weighted sum. The

305 scattering scheme must use sufficient zenith angle quadrature points to represent
306 the phase functions of the scattering particles. Second, as thermal scattering is an
307 azimuthally symmetric process, only the first (azimuthally-independent) Fourier
308 component was used. The numerical calculations involved in multiple scattering
309 are computationally expensive, slowing the retrieval process by an order of mag-
310 nitude, but has a significant effect on the 5- μm window of the VIMS spectrum
311 (Section 4).

312 3.4. Introducing Cloud Models

313 As knowledge of Saturn's vertical cloud structure and optical properties re-
314 mains rather limited, we aimed to explore a broad range of parameter space with
315 a variety of different cloud models (Table 3). A full vertical opacity retrieval
316 was poorly constrained by the 5- μm data due to the degeneracy between PH_3 and
317 aerosols. Instead, four parameterised vertical structure models were considered
318 (optical depths are quoted for 5 μm);

- 319 • **I: Single Compact Cloud:** A single aerosol layer with variable optical
320 thickness τ_1 and base pressure, p_b .
- 321 • **II: Two Compact Clouds:** A compact aerosol layer with a variable τ_1 ,
322 composition and base pressure was placed beneath a spectrally-grey cloud
323 at a fixed altitude with variable opacity, τ_2 . This upper cloud was arbitrarily
324 placed at the predicted NH_3 condensation altitude for a solar nitrogen abun-
325 dance (1.47 bar, 152 K, Atreya et al., 1999) to minimise the number of free
326 parameters in the model, although it would be deeper for bulk enrichments
327 in Saturn's nitrogen content.

- 328 • **III: Single Extended Cloud:** A well-mixed distribution of aerosols with
329 variable opacity τ_1 between the 100-mbar pressure level (the tropopause)
330 and a variable base pressure, p_b .
- 331 • **IV: Compact Upper Cloud, Extended Deep Cloud:** A combination of
332 the physically-thin upper cloud from Model II and the extended cloud from
333 Model III.

334 In addition to the vertical structure, we tested the sensitivity to the aerosol
335 composition by calculating extinction cross sections and phase functions $p(\theta)$
336 based on the refractive indices in Table 3 and shown graphically in Fig. 3. The
337 models tested were (A) a grey cross-section and single scattering albedo ($\omega_0 =$
338 0.95) across the 4.6-5.1 μm range, with an isotropic phase function (Fig. 4); (B)
339 pure NH_3 ice (Martonchik et al., 1984); (C) pure NH_4SH (Ferraro et al., 1980);
340 (D) a modified pseudo- NH_4SH cloud based on a refractive index of $2.3 + 0.01i$
341 (following suggestions by, Nixon et al., 2001); and (E) updated NH_4SH optical
342 constants from Howett et al. (2007). For each cloud type in Table 3, Mie theory
343 was used to calculate the scattering properties of spherical 1- μm -radius particles
344 with a standard gamma distribution of particle sizes, variance 0.05 μm . The phase
345 function $p(\theta)$ (shown in Fig. 4) was calculated as a two-term Henyey-Greenstein
346 (HG) function (explicitly calculating the fraction of forward scattering and the
347 asymmetries in the forward and backward scattering functions). With the ex-
348 ception of the isotropic scatterer, there is little to distinguish between the phase
349 functions in Fig. 4, which are mostly determined by the chosen particle size. The
350 crucial differences between the cloud models lies in the wavelength-dependence
351 of the single scattering albedo (Fig. 3d, related to the imaginary refractive indices
352 in Fig. 3a).

353 The absorption cross-sections, HG phase functions and size distributions in
354 Figs. 3 and 4 were not intended to be an exhaustive representation of Saturn's
355 clouds, given the substantial degeneracies inherent in the interpretation of VIMS
356 spectra. Nevertheless, they are broadly representative of the types of condensed
357 phases that might be present in Saturn's troposphere. Addition of further com-
358 plexity (e.g., using the dual-absorber of NH_3 and NH_4SH following Sromovsky
359 and Fry, 2010a, , or introduction of non-spherical particles) was not warranted
360 by the 4.6-5.1 μm data, but such a combination is certainly possible for Saturn's
361 cloud decks. Hydrazine (N_2H_4), from the photolysis of tropospheric NH_3 , is not
362 expected to be a major constituent of the tropospheric clouds, and the single scat-
363 tering albedo and phase function in Figs. 3 and 4 (Clapp and Miller, 1996) are
364 not sufficiently different in the 4.6-5.1 μm range to distinguish hydrazine from
365 NH_3 ice in the VIMS spectrum. However, one important species is absent from
366 Table 3 that could potentially be a major contributor to IR opacity in this spectral
367 range - diphosphine (P_2H_4), which is expected to be present in significant quanti-
368 ties from PH_3 photolysis. Very little is known about the absorptive and scattering
369 properties of P_2H_4 , and a determination of the optical properties of diphosphene
370 is an urgent priority for future VIMS studies, particularly in reflected sunlight.
371 The uncertain spectral properties of non-spherical particles, $\text{NH}_3+\text{NH}_4\text{SH}$ mixes,
372 P_2H_4 and other potential contaminants in Saturn's clouds could significantly alter
373 the retrieved opacities and cloud altitudes described in Section 5. Nevertheless,
374 useful latitudinal contrasts in atmospheric parameters can still be derived.

375 3.5. Sensitivity Analysis

376 Synthetic spectra for each gas contributing to the 5- μm window are presented
377 in Fig. 5. The mole fractions in the reference atmosphere were scaled by arbitrary

378 amounts to show their spectral influence (using a simple compact grey cloud,
379 model II.A). PH_3 , NH_3 and AsH_3 have the largest contributions to this range,
380 with smaller influences from H_2O , GeH_4 , CO and CH_3D . PH_3 in particular has
381 a strong effect on the mean flux and spectral gradient between 4.9 and 5.0 μm .
382 Variations of CH_4 and $^{13}\text{CH}_4$ have negligible effects on the spectra. Some of
383 the spectral signatures are similar (e.g., AsH_3 and GeH_4 , not to mention those of
384 aerosol absorption and the broad effects of PH_3), leading to degeneracies in the
385 interpretation of VIMS spectra, which will be explored below.

386 The vertical sensitivity of the spectra is highly dependent on the scattering
387 properties and opacity of the cloud layers as well as the abundances of the absorb-
388 ing gases. However, an estimate of the sensitivity is provided by the functional
389 derivatives for the best-fitting II.A model (Fig. 6, using compact clouds at 1.4
390 and 2.7 bar and $\tau_1 = \tau_2 = 1$). The functional derivatives have been normalised,
391 so that no account has been made for the magnitude of their spectral effects from
392 Fig. 5. VIMS spectra are generally sensitive to abundance profiles in the 1-6 bar
393 region, with peak sensitivity for PH_3 , NH_3 and AsH_3 in the 1-3 bar range. Some
394 gases (notably GeH_4 , CO and CH_3D) show sensitivity to the 0.4-1.0 bar range,
395 although these generally have a smaller overall effect on the spectrum. In the ab-
396 sence of absorbing cloud layers, contribution functions (Fig. 7, the product of
397 the transmission weighting function, $d\tau/dz$, and the black body emission, $B(z, T)$)
398 demonstrate that Saturn's thermal emission originates from the 4-6 bar region,
399 where atmospheric temperatures reach approximately 240 K. In the absence of
400 absorbing/scattering aerosols, the radiance in the 5- μm window would therefore
401 be considerably larger than the 140-190 K brightness temperatures in Fig. 2.

402 4. Model Degeneracies and Validation

403 Modelling a single VIMS spectrum is relatively straightforward - a large num-
404 ber of gaseous and aerosol parameters can be tuned to provide an excellent fit to
405 the low resolution VIMS spectra ($R \approx 330$ at $5 \mu\text{m}$). However, the results must
406 also be physically realistic when multiple retrievals are performed to study Sat-
407 urn's zonal mean properties. Furthermore, the residuals between measured and
408 synthetic spectra (the χ^2 parameter) should be as spatially uniform as possible to
409 ensure that we have captured all of the variability in the model. This section will
410 explore the degeneracies inherent in modelling VIMS nightside spectra in the ab-
411 sence of prior constraints on Saturn's aerosol optical properties and distributions.
412 Through extensive tests of the model with different temperature, composition and
413 cloud assumptions with the 22 coarse zonal-mean spectra described in Section 2.2,
414 we demonstrate that VIMS data can provide robust conclusions about *relative* spa-
415 tial variability, even if *absolute* abundances and opacities are poorly constrained.

416 4.1. Model Assumptions

417 We began by testing a number of assumptions in our forward models and re-
418 trievals. The simplest solution would be to fit the spectrum by varying $T(p)$ or PH_3
419 alone, in the absence of attenuating/scattering aerosols. However, thermal varia-
420 tions needed to be unrealistically large in the 1-5 bar region to reproduce the cool
421 brightness temperatures observed in Fig. 2, and it proved impossible to reproduce
422 the 4.6-4.9 μm and 4.9-5.1 μm regions simultaneously by varying PH_3 alone. Fur-
423 thermore, fixing all the gases at their *a priori* distributions and varying the opacity
424 of the simplest cloud model (I.A, a single compact grey-absorbing cloud in Table
425 3) failed to reproduce the spectrum. The VIMS spectra can only be reproduced by

426 a simultaneous retrieval of gaseous abundances and aerosol opacity.

427 *But which gases to include in the retrieval?* With the best-fitting aerosol distri-
428 bution in the grey-absorbing case (both scattering and non-scattering), we sequen-
429 tially added scaled retrievals of each gas (i.e., fixing the vertical profile but varying
430 the absolute abundance) and assessed (a) the quantitative improvement to χ^2 and
431 (b) the qualitative appearance of the meridional distribution from the 22 spectra.
432 Variations of PH_3 were essential, whereas the importance of NH_3 only became
433 apparent once we investigated equatorial latitudes where the spectrum near 5.1
434 μm appears markedly different from other regions (Fig. 2). The addition of AsH_3
435 moderately improved the fit in the region surrounding the broad absorption at 4.74
436 μm (this was especially true at low latitudes). However, although the remaining
437 gases in the model (GeH_4 , CO , H_2O and CH_3D) had some minor effects on the
438 spectra, they did not deviate far from their *a priori* abundances and were deemed
439 insignificant (using an F-statistic test, Bevington and Robinson, 1992). Omitting
440 these four gases from the retrieval had negligible effects on the retrieved NH_3 , PH_3
441 and AsH_3 abundances.

442 *Adding complex cloud parameterisations:* Simultaneously fitting for the spa-
443 tial variation of PH_3 , NH_3 and AsH_3 , along with the variable opacity and depth
444 of the single-cloud model I.A failed to provide adequate fits to the VIMS spectra.
445 A similar conclusion was reached for Galileo/NIMS $5\text{-}\mu\text{m}$ spectra of Jupiter (e.g.,
446 Irwin et al., 2001), which required two separate aerosol populations, suggestive
447 (but not uniquely) of a main jovian cloud deck of NH_4SH overlain by optically thin
448 NH_3 clouds. This prompted the development of the 3 additional cloud models (II-
449 IV) in Section 3.4 which immediately improved the fits to the VIMS spectra. The
450 2-cloud schemes produced the best fits as the two opacity sources were allowed

451 to vary independently of one another, increasing the number of free parameters
452 available for the retrieval. In addition, experiments varying both the deep cloud
453 base pressure (p_b) and opacity (τ_1) showed that they have sufficiently different
454 spectral effects to make them separable. A comparison of the χ^2 values in Section
455 4.2 for the four different vertical models show that, while some can be ruled out,
456 others gave such similar spectral results that they could not be distinguished from
457 each other. Furthermore, the VIMS spectra are insensitive to location and extent
458 of the upper cloud in models II and IV - shifting the base pressure between 1.4
459 and 1.8 bar for both compact and extended upper clouds had no effect on the fitted
460 spectra, only the cumulative opacity (τ_2) has an influence.

461 *Temperature variations in the deep troposphere:* Independent retrievals of
462 $T(p)$ from the 5- μm window would be impossible given the degeneracy with
463 PH_3 and aerosols, although spatial variations are expected to be small. Never-
464 theless, three different assumptions were tested: (a) a mean CIRS-derived $T(p)$
465 from Cassini's prime mission (Fletcher et al., 2009a) with the same lapse rate
466 g/c_p for all latitudes; (b) the same mean $T(p)$ but with a latitude-dependent lapse
467 rate (i.e., varying with g); and (c) the full meridional CIRS $T(p)$ with a latitude-
468 variable lapse rate. The last assumption provided the best fits to the VIMS spectra
469 (there is VIMS sensitivity to $p < 800$ mbar in Figs. 6 and 7), although in prac-
470 tise there was little to differentiate between the three cases. Retrieved meridional
471 distributions of NH_3 and AsH_3 were very similar for all three assumptions, but
472 PH_3 and aerosol optical depths were affected. North-south asymmetries of PH_3
473 and aerosols were present for all three cases, but the PH_3 asymmetry was smaller
474 when the CIRS-derived tropospheric temperature asymmetry was accounted for.
475 Uncertainties in retrieved absolute values arising from the differing temperature

476 assumptions are 13%, 16% and 10% for PH_3 , NH_3 and AsH_3 , respectively; 33%
477 and 50% for the deep and upper cloud opacities. Thus the retrieved gaseous com-
478 position and aerosols have a degeneracy with the deep atmospheric temperatures,
479 but the best-fitting assumption (c) was used for the remainder of this study.

480 *Vertical distribution of PH_3 :* Early models of VIMS spectra (e.g., Baines
481 et al., 2009) assumed PH_3 to be well-mixed up to 0.55 bar (Fletcher et al., 2009a).
482 However, it proved difficult to simultaneously fit the 4.6-4.7 μm radiances and
483 the 4.8-5.0 μm spectral gradient. Fixing the PH_3 abundance at some mean for all
484 latitudes generally worsened the quality of the spectral fits, particularly over the
485 southern hemisphere (PH_3 was noted to be elevated in the southern troposphere,
486 Fletcher et al., 2009a). Finally, we parameterised the vertical PH_3 distribution
487 in terms of a deep mole fraction (q_0) up to a pressure level (p_0), followed by a
488 decreasing abundance with altitude according to a fractional scale height, (f , the
489 ratio of the gas scale height to that of the bulk atmosphere) (Fletcher et al., 2007a).
490 Varying p_0 simultaneously with aerosols and other gaseous mole fractions for all
491 22 VIMS spectra (in both the scattering and non-scattering cases), we found opti-
492 mum fits for p_0 between 1.1-1.3 bar (examples of the χ^2 surfaces for the equator,
493 30°N and 30°S are shown in Fig. 8). The cloud base and PH_3 p_0 were found to be
494 at lower pressures (higher altitudes) at the equator than at mid-latitudes.

495 The introduction of the parameterised PH_3 profile had a substantial effect on
496 the χ^2 at all latitudes, producing closer fits to both the 4.6-4.7 μm region and the
497 spectral gradient between 4.8-5.0 μm . Similar tests for NH_3 and AsH_3 indicated
498 that the well-mixed assumption was perfectly valid. However, the PH_3 p_0 de-
499 termined by VIMS was considerably deeper than that determined by CIRS and
500 sub-mm data (0.55-0.65 bar, Orton et al., 2000; Fletcher et al., 2009a). Further-

501 more, the retrieved fractional scale height was rather small, permitting negligible
502 PH₃ abundances at $p < 1$ bar, again inconsistent with CIRS. Indeed, when we
503 compared the range of PH₃ abundances derived from VIMS (3.0-5.5 ppm for the
504 range of cloud models studied here, Section 5) to that derived from CIRS (5.4-8.2
505 ppm, with a mean of 6.4 ppm, Fletcher et al., 2009a), we found that VIMS and
506 CIRS PH₃ abundances differed by factors of 1.5-1.8, even though the meridional
507 variations of q_0 and f were similar from both instruments. Although CIRS is sen-
508 sitive to lower pressures (300-800 mbar) than VIMS (2-3 bar), we expect PH₃ to
509 be well-mixed between these two levels. It is unlikely that near-IR line strengths
510 could be too strong by a factor of two, as this exceeds the uncertainties on line data
511 for either the near-IR or mid-IR vibrational bands (Section 3.2). Identification of
512 the source of this discrepancy will require (i) consistent measurements of PH₃ line
513 data across multiple bands; (ii) higher spectral resolution observation of Saturn's
514 emission to separate PH₃ absorption from continuum opacity sources; and (iii)
515 simultaneous near and mid-IR retrievals in the presence of tropospheric aerosols.
516 Nevertheless, *relative* PH₃ variations can still be derived from VIMS spectra.

517 4.2. Degeneracies in Spectral Modelling

518 At the start of this analysis, it was hoped that VIMS nightside spectra would
519 constrain a unique cloud model and, independently, the spatial distribution of
520 gases. However, the degeneracies between the different model parameters soon
521 became overwhelming. Fig. 9 shows the meridional distribution of χ^2 for all four
522 vertical models (I-IV), scattering and non-scattering cases, for optical models A-C
523 (Figs. 3-4). Testing of models D (pseudo-NH₄SH cloud of Nixon et al., 2001) and
524 E (updated NH₄SH optical constants by Howett et al., 2007) produced negligible
525 differences to (i) the quality of the spectral fits and (ii) the meridional distributions

526 of gases and aerosols, so were omitted from the subsequent analysis. All cloud
527 models produce poor fits poleward of 55°N due to a failure of our models to fit the
528 higher emission angles (sensitive to higher altitudes in Saturn's atmosphere).

529 In general, the compact cloud models I and II produced the best fits to the spec-
530 tra. The 2-cloud scheme fitted better at the equator (Fig. 9); at latitudes poleward
531 of 10°S and the $35\text{-}65^{\circ}\text{N}$ region of the northern hemisphere. However, the 2-cloud
532 scheme cannot be distinguished from the single cloud scheme between $10\text{-}35^{\circ}\text{N}$,
533 in a region where haze opacity is thought to be negligible (see Section 5). Finally,
534 although the extended deep cloud models (III and IV) produced reasonable fits
535 to the spectrum by eye, the χ^2 (Fig. 9) was sufficiently different to distinguish
536 between the compact and extended cloud structures for the deep cloud.

537 In the non-scattering case, the residuals for optical models A-C (the grey, NH_3
538 and NH_4SH cloud compositions) were indistinguishable from one another. Mod-
539 elling scattering within the clouds improved the fits for the grey isotropic scatterer
540 and NH_4SH clouds, but not for NH_3 (although differences in the chosen particle
541 sizes could have an effect on this conclusion). Ruling out pure NH_3 ice, the two
542 remaining optical models produced very similar fits to the VIMS spectra: the grey
543 assumption was better at northern mid-latitudes ($10\text{-}40^{\circ}\text{N}$) whereas solid NH_4SH
544 provided a better fit at all other latitudes (Fig. 9). Although this is certainly not
545 a unique solution, the NH_4SH imaginary refractive indices in Fig. 3 from both
546 Ferraro et al. (1980) and Howett et al. (2007) suggest smaller single scattering
547 albedos between 4.7 and $4.9 \mu\text{m}$ compared to NH_3 ice or the other possible cloud
548 compositions, even though the scattering phase functions (Fig. 4) are all very
549 similar to one another. This difference provides marginally better fits for solid
550 NH_4SH than other constituents, although we have not conducted an exhaustive

551 study of possible cloud candidates (e.g., the omission of diphosphine described in
552 Section 3.4). In conclusion, the compact scattering cloud schemes (models I and
553 II, with II doing better at known ‘hazy’ latitudes), in combination with the grey or
554 NH_4SH optical properties (A and C) provided the best reproductions of the VIMS
555 spectra.

556 4.2.1. Aerosol Profile Uncertainties

557 Given that no single cloud model provided the best fits to the data, we have
558 to consider the range of possible solutions to this underconstrained problem. If
559 compact cloud layers are used (models I-II), the base pressures for the opacity
560 (p_b) must be placed between 1.9 and 2.7 bar. In the southern hemisphere, where
561 the opacity of the upper cloud is highest, p_b is poorly constrained and can be at
562 any pressure greater than 2 bar (see the χ^2 figures at the top of Fig. 12). Extended
563 well-mixed clouds in the deep troposphere (models III-IV, previously shown to
564 give poor reproductions of the VIMS data) require $p_b > 2.8$ bar, and typically
565 place the bottom of the cloud between 3.3 and 4.0 bar.

566 The addition of scattering to the model causes the retrieved optical depths of
567 the deep cloud (τ_1) and upper cloud (τ_2) to increase by factors of 2-5 relative to
568 the non-scattering case (depending on the chosen optical model, Fig. 10). Fur-
569 thermore, scattering introduces an emission-angle dependence to the deep optical
570 depths if the cloud is an isotropic grey scatterer (Fig. 10a), but not when it is com-
571 prised of solid NH_4SH (Fig. 10b). As the emission angle is varying from equator
572 to pole, this suggests that the isotropic phase function (Fig. 4) is a poor representa-
573 tion of Saturn’s aerosols, as previous reflected sunlight studies of Saturn’s clouds
574 suggest a latitudinally-uniform τ_1 or an equator-to-pole decrease in opacity (e.g.,
575 Stam et al., 2001; Karkoschka and Tomasko, 2005). The NH_4SH scattering cloud

576 produced optical depths for the deep cloud which were largely independent of
577 latitude (Fig. 10b). Ultimately the meridional variation of τ_1 cannot be uniquely
578 determined unless (i) each latitude is viewed with the *same* emission angle; or (ii)
579 multiple emission angles are used to separate the degenerate effects of emission
580 angle and τ_1 . No emission angle dependence is detected in retrievals of the upper
581 cloud, τ_2 (Fig. 10c), which shows an asymmetry between northern and south-
582 ern hemispheres for all of the cloud models tested (models II and IV featured the
583 upper cloud), although the retrieved optical depths are highly dependent on the
584 chosen aerosol model.

585 4.2.2. Degeneracies in Gaseous Composition

586 Unfortunately, the degeneracy between the different cloud models provides
587 substantial uncertainties in the absolute abundances of gases derived from the
588 5- μm window. The *relative* variations of ammonia (shown in Fig. 11a for the
589 grey-cloud optical model) are similar for all cloud models, but there are clear off-
590 sets in *absolute* abundance. The use of scattering clouds increases the pathlength
591 for individual photons in the upper troposphere, and hence reduces the amount of
592 each gas necessary to reproduce the absorption features (grey curves in Fig. 11
593 are systematically lower than the black non-scattering curves). Compact cloud
594 models tend to yield smaller retrieved abundances than extended clouds, and even
595 the best-fitting aerosol models differ in abundance by a factor of 2-3. Neverthe-
596 less, the enhanced NH_3 abundances at 45°N, 25°S and the equator are persistent
597 features, irrespective of the chosen cloud model.

598 However, in the cases of AsH_3 and PH_3 , the chosen cloud model can have a
599 substantial effect on both the meridional structure and the absolute abundances.
600 AsH_3 (Fig. 11b) shows a north-south asymmetry in the non-scattering case that

601 becomes much smaller when multiple scattering in the southern hemisphere is
602 taken into account. The distribution of PH_3 is even more problematic, with a large
603 scatter in measured abundances (Fig. 11c), although each aerosol model generally
604 produces a north-south asymmetry in PH_3 . The formal retrieval error on each
605 PH_3 measurement is small, given that this gas dominates the shape of the VIMS
606 spectrum, but the degeneracy between the cloud models makes a determination of
607 the absolute abundance near-impossible without additional constraints.

608 The cause of this offset in absolute abundance is demonstrated in Fig. 12 for
609 15°N , 15°S and the equator (using non-scattering cloud model II.A), which shows
610 how the algorithm converges to the optimal solution. There is a large variation
611 of retrieved parameters with the cloud base pressure, showing how sensitive the
612 absolute abundances are to the choice of aerosol model. As we described above,
613 the deep cloud base pressure for the southern hemisphere (with the thickest upper
614 cloud) is poorly constrained and could be placed anywhere at $p > 2$ bar (first row
615 of Fig. 12). Placing cloud opacity at greater depth requires larger abundances of
616 PH_3 (2nd row) and NH_3 (7th row), but smaller abundances of AsH_3 (6th row) to
617 reproduce the absorption features. Furthermore, any variations in the deep cloud
618 opacity τ_1 are largely compensated by the upper cloud τ_2 (4th and 5th rows of Fig.
619 12). This figure demonstrates the tradeoffs between the parameters in retrievals at
620 each latitude, so we conclude that the *absolute* abundances and optical depths are
621 dependent on the correct parameterisation of Saturn's clouds.

622 4.3. Validation Experiments

623 A robust way of demonstrating the validity of the retrieval scheme is to at-
624 tempt extraction of the same variables from modelled VIMS spectra with simu-
625 lated noise. 200 spectra were synthesised with non-scattering cloud model II.A

626 at a range of latitudes ($\pm 45^\circ$) and emission angles (0-45°); a range of *a priori*
627 abundances for PH₃, NH₃, AsH₃ and GeH₄ (the latter as a control); and a range
628 of values for the deep cloud τ_1 and p_b and upper cloud τ_2 . The synthetic spectra
629 were randomised using the same noise levels described for the real VIMS spec-
630 tra (Section 2.1), and then the parameters were simultaneously retrieved from the
631 synthetic spectra. Fig. 13 shows a positive correlation between the true values
632 and retrieved values for each parameter, with the exception of GeH₄. The average
633 deviations between modelled and retrieved values are: PH₃ (8%), AsH₃ (7.3%),
634 NH₃ (30%), τ_1 (59%), τ_2 (25%) and p_b (17.6%). In addition, the NH₃ abundance
635 appeared to be 30% lower than the true values, whereas the retrieved τ_1 was 54%
636 larger than the input values. The large uncertainties on τ_1 , τ_2 and p_b demonstrate
637 the high correlation between these parameters, and the difficulties in separating
638 them in the retrievals.

639 These simple experiments provide estimates of the uncertainties in absolute
640 abundances based solely on random measurement errors. They do not represent
641 the uncertainties due to systematic offsets. As we have seen, abundance uncer-
642 tainties are dominated by the choice of cloud parameterisation rather than random
643 error on the VIMS spectra. Relative spatial variability in retrieved quantities are
644 more robust, and these will be presented in Section 5.

645 5. Results

646 Atmospheric composition (parameterised PH₃; well-mixed NH₃ and AsH₃)
647 and aerosol properties (τ_1 , τ_2 and p_b using the 2-cloud scheme, model II) were
648 retrieved from 107 VIMS 4.6-5.1 μm spectra between 38°S and 67°N (planeto-
649 centric). The meridional distribution of each parameter is shown in Fig. 14, with

650 the zonal mean radiances and brightness temperatures at $5\ \mu\text{m}$ indicated in the top
651 panels and the best-fitting spectral models in Fig. 15. Given the difficulties in dis-
652 tinguishing between scattering and non-scattering cases with the grey or NH_4SH
653 optical properties (models A and C) based on the χ^2 alone (Fig. 14b), we applied
654 both techniques to the VIMS retrievals. Pure NH_3 ice and isotropic scattering
655 were previously ruled out, although we stress that the retrieved atmospheric com-
656 position was very similar in these cases. The meridional distribution of χ^2 (Fig.
657 14b) shows a small improvement using multiple scattering with the phase function
658 of NH_4SH , but the effect is insignificant within a $\Delta\chi^2 = 1$. Although the scattering
659 cloud is more physically realistic, its inclusion has a substantial effect on retrieved
660 parameters for such a small improvement in χ^2 , so both sets of results are shown
661 to highlight the degeneracy issue.

662 5.1. Saturn's Clouds

663 The retrieved properties of the compact cloud scheme are shown in Fig. 14c-e.
664 The base pressure of the deep cloud is poorly constrained in the southern hemi-
665 sphere where significant opacity due to aerosols in the upper cloud (Fig. 14c) and
666 PH_3 (Figs. 14g-h) prevent a unique determination of the deep cloud base. The
667 equatorial cloud is allowed to be present at lower pressures (approximately 2.1
668 bar) in the non-scattering case, compared to high pressures of the northern hemi-
669 sphere cloud deck (2.5-2.8 bar). The need for this 2.1-bar equatorial cloud is re-
670 moved when multiple scattering is used, when the equatorial cloud base becomes
671 consistent with northern mid-latitudes. Both the scattering and non-scattering
672 models agree on the cloud base pressures at northern mid-latitudes. Seasonally-
673 variable cloud opacities in the 2-3 bar region are deemed unlikely given the long
674 radiative timescales at these pressures, so a cloud base in the 2.5-2.8 bar region is

675 likely to exist globally on Saturn, with upward advection pushing the cloud higher
676 at the equator.

677 Optical depths of the two clouds are higher in the multiple scattering case.
678 The upper cloud τ_2 (arbitrarily placed at 1.4 bar, representative of the cumula-
679 tive opacity of clouds and hazes above this pressure level) is more opaque in the
680 southern hemisphere in both scattering and non-scattering cases. It is likely that
681 the extended haze layers between the tropopause and 1.4 bar that are responsible
682 for scattering of reflected sunlight on the dayside (Pérez-Hoyos et al., 2005) are
683 also contributing to the attenuation of 5- μ m flux on the nightside. Finally, the up-
684 per cloud shows enhanced equatorial opacity only in the multiple-scattering case.
685 Increased equatorial opacity is qualitatively expected when we consider the ‘hazy’
686 appearance of Saturn’s low latitudes in reflected sunlight (e.g., Porco et al., 2005;
687 Vasavada et al., 2006) and the observations of vertical upwelling of the disequi-
688 librium species PH₃ (Fletcher et al., 2009a).

689 The deep cloud opacity (Fig. 14d) shows opposing behaviours depending on
690 the scattering assumptions. In the scattering case, we see a trend of increased
691 opacity at high latitudes, whereas the opposite is true in the non-scattering case.
692 A mean of the two would be uniform with latitude, which may be more realistic for
693 the non-seasonal conditions in the 2-3 bar pressure regime. Small-scale variations
694 in τ_1 of approximately 20-30% are colocated in the two cases, but the amplitude
695 of the opacity variation is likely to depend on the spatial resolution of the VIMS
696 images. Comparing to Fig. 1, the narrow axisymmetric bands of bright 5- μ m
697 flux are coincident with regions of lower opacity (particularly evident between 20-
698 30°N). Fig. 14d suggests that these bright bands are regions of diminished opacity
699 of the deep cloud layer, rather than being due to changes in the base pressure of the

700 2.5-2.8 bar cloud or the opacity of the upper ‘haze’. Finally, unlike the elevated
701 opacity of the upper cloud at low latitudes, there is nothing notable about the deep
702 cloud opacity at the equator.

703 In summary, VIMS nightside spectra are consistent with clouds in two regimes
704 - (i) a compact, meridionally-uniform cloud deck centred in the 2.5-2.8 bar region
705 with small-scale opacity variations responsible for the narrow, bright axisymmet-
706 ric lanes in VIMS images; and (ii) a hemispherically-asymmetric upper cloud
707 above 1.4 bar, whose exact altitude and vertical structure are not constrained by
708 VIMS, but which is likely to extend towards the tropopause and is responsible for
709 reflected sunlight scattering. The upper cloud/haze is seasonally variable, whereas
710 the deep cloud is not. Degeneracy between the scattering and non-scattering cases
711 leads to uncertainties in absolute optical depths, and elevated equatorial opacity is
712 only present in the scattering case.

Finally, although a 2.5-2.8 bar cloud deck of NH_4SH provided the best fits to the spectra for the limited range of clouds tested in this study, this solution is certainly non-unique and we cannot rule out a more complex combination of NH_3 , NH_4SH and possibly P_2H_4 (see Section 3.4). The cloud deck is deeper than the predicted condensation altitudes for pure NH_3 (1.47-1.81 bar, Table 4 of Atreya et al., 1999, for solar and five-fold enrichments of heavy elements), but also higher than the predicted levels of NH_4SH (4.56-5.72 bar). Homogeneous cloud condensation occurs when the partial pressure of a gas exceeds its saturation vapour pressure. Formation of solid NH_4SH is more complex, involving a two-component reaction between NH_3 and H_2S whose equilibrium can be expressed by the empirical equation (Lewis, 1969; Atreya, 1986);

$$\log(p_{\text{NH}_3} p_{\text{H}_2\text{S}}) = 14.82 - \frac{4705}{T} \quad (1)$$

713 where p_{NH_3} and p_{H_2S} are the partial pressures of the two gases. Assuming that the
714 abundances of the two gases are equal at the cloud condensation altitude (H_2S is
715 completely used up in this reaction, whereas NH_3 survives to condense at higher,
716 cooler altitudes), and comparing the saturated vapour pressure curve to Saturn's
717 temperature profile, we require approximately 2 ppm of H_2S to form the VIMS
718 2.5-2.8 bar cloud. This would be produced by only 10% of the solar S/H ratio
719 of Grevesse et al. (2007), considerably smaller than the $10\times$ solar S/H abundance
720 suggested by Briggs and Sackett (1989) (equivalent to 250 ppm), but larger than
721 the 16 ppb upper limit of Weisstein and Serabyn (1996). Simple thermodynamic
722 theory is a poor approximation to Saturn's true clouds, given that they are unlikely
723 to be pure ice condensates and probably contain a range of impurities. The VIMS
724 2.5-2.8 bar cloud cannot be identified unambiguously using the present dataset.

725 5.2. Gaseous Composition

726 Figs. 14g-j show the meridional distributions of PH_3 , NH_3 and AsH_3 in the
727 scattering and non-scattering cases. In all three cases scattering increases the path
728 length of individual photons and hence reduces the abundances required to repro-
729 duce the absorption features.

730 5.2.1. Phosphine

731 Section 4 demonstrated the uncertainties in the meridional distribution of phos-
732 phine under different scattering assumptions. The fractional scale height (repre-
733 senting the abundance for $p < 1.3$ bar) shows a local maximum at the equa-
734 tor under non-scattering conditions, consistent with the distribution identified by
735 Cassini/CIRS in the 0.1-0.8 bar region (Fig. 7 of Fletcher et al., 2009a). Further-
736 more, VIMS successfully reproduces the mid-latitude asymmetry in the fractional

737 scale height, the local minimum at 10-20°S and the rising abundance towards
738 40°S observed by CIRS. The asymmetry in the fractional scale height at higher
739 altitudes may be due to enhanced shielding by southern-hemisphere aerosols, in-
740 creasing photolysis lifetimes in the south and allowing PH₃ to accumulate over
741 the summer/autumn season.

742 But there are problems with these PH₃ results: (i) the knee pressure of the
743 distribution ($p_0 = 1.3$ bar) is considerably deeper in the VIMS retrievals than
744 the CIRS retrievals ($p_0 = 0.55$ bar); (ii) the deep mole fractions in the scatter-
745 ing (mean and standard error 3.1 ± 0.3 ppm) and non-scattering (4.4 ± 0.6 ppm)
746 cases are smaller than the 6.4 ± 0.4 ppm mole fraction reported by CIRS (Fletcher
747 et al., 2009a); (iii) both the scattering and non-scattering cases feature a local min-
748 imum in the deep ($p > 1.3$ bar) equatorial abundance which was not observed by
749 CIRS (CIRS is insensitive to $p > 0.8$ bar); and (iv) the need for the equatorial
750 enhancement in the fractional scale height is removed by the inclusion of scatter-
751 ing. Indeed, on the last point it seems that the PH₃ fractional scale height and the
752 τ_2 of the upper cloud have exchanged roles in the retrievals, indicating a degen-
753 eracy between the two variables. The VIMS-derived mole fraction is also smaller
754 than the disk-averaged 4.5-7.5 ppm range reported for Saturn's deep troposphere
755 by Burgdorf et al. (2004), Lellouch et al. (2001), Orton et al. (2000), de Graauw
756 et al. (1997) and Noll and Larson (1990). Finally, an asymmetry in the deep PH₃
757 abundance in the non-scattering case is deemed unlikely as the vertical mixing
758 processes responsible for the presence of this disequilibrium species in the upper
759 troposphere are not expected to be seasonally-variable. No deep asymmetries are
760 observed in the multiple-scattering case.

761 Tests revealed that the use of the CIRS-derived mole fractions and p_0 could not

762 reproduce the VIMS spectrum adequately for any choice of cloud model, which
763 leaves us with a conundrum - even though the meridional distributions are largely
764 similar, the absolute values are quite different from the two instruments. As the
765 same retrieval model was used in both studies, one possibility is that the line data
766 for the pentad polyad at $5\text{-}\mu\text{m}$ are inconsistent with that of the dyad at $9\text{ }\mu\text{m}$, mak-
767 ing direct comparisons difficult. Indeed, the $5\text{-}\mu\text{m}$ line data are only accurate to
768 the 20-30% level (Section 3.2), which may explain some of the discrepancy, but
769 not all of it. Furthermore, just as VIMS retrievals are prone to PH_3 and aerosol
770 degeneracies, CIRS retrievals are prone to $T(p)\text{-PH}_3$ degeneracies. Finally, the
771 retrieved high-altitude PH_3 is determined by the absorption complex at $4.74\text{-}\mu\text{m}$:
772 if scattered light within the instrument artificially enhances the flux in this ab-
773 sorption band (see Section 2.1) then we would require less PH_3 than expected
774 from CIRS. Further testing of the PH_3 -aerosol degeneracy with improved knowl-
775 edge of the cloud composition, along with consistent measurement of the PH_3 line
776 data, is required to resolve this issue.

777 If we take the VIMS-derived PH_3 at face value, then some mechanism must
778 be depleting PH_3 above the $p_0 = 1.3\text{-bar}$ level. PH_3 is thought to be well-mixed
779 by vertical diffusion at depth and depleted at higher altitudes due to photolysis to
780 diphosphine (P_2H_4 , a candidate for Saturn's haze) and elemental phosphorous. In
781 the 1-3 bar region of VIMS sensitivity (Fig. 6), photochemical models suggest that
782 production and loss rates are balanced due to recycling of P_2H_4 to PH_3 (J. Moses,
783 *pers. comms.*), so depletion would be unexpected. If the PH_3 loss at $p < 1.3\text{ bar}$
784 is real, then it may simply represent adjustment of the vertical profile between the
785 well-mixed deep profile and the photolysis regime.

786 5.2.2. *Ammonia*

787 Unlike PH_3 , the meridional distribution of NH_3 was similar for all of the
788 aerosol models tested, even though the absolute abundances vary between scatter-
789 ing and non-scattering cases in Fig. 14i. Indeed, the largest discrepancy between
790 scattering and non-scattering is at the equator and mid-southern latitudes, where
791 the aerosol opacity was at its largest. NH_3 is enhanced at the equator between $\pm 5^\circ$
792 latitude by three times the northern mid-latitude abundances. This enhancement
793 is coincident with the narrow region of diffuse brightness in Fig. 1, and with a
794 narrow prograde jet identified by García-Melendo et al. (2010) which exists in ad-
795 dition to the broad equatorial jet. However, the NH_3 enhancement is confined to a
796 much narrower equatorial region ($\pm 5^\circ$) than the CIRS-derived PH_3 enhancement
797 ($\pm 20^\circ$) in the 0.2-0.8 bar region (Fletcher et al., 2009a).

798 Smaller enhancements are also notable in axisymmetric bands at 23-25°S and
799 42-47° (planetocentric), coinciding with dark lanes at 5.1 μm (Fig. 1). The north-
800 ern hemisphere NH_3 peak exists between opposing zonal jets (prograde at 41°N,
801 retrograde at 49°N), suggesting upwelling on the poleward side of the prograde
802 jet. Interestingly, this jet was the location of a meandering lane known as the
803 ribbon wave, first discovered by Voyager (e.g., Godfrey and Moore, 1986). The
804 region north of the jet exhibited significant eddy activity associated with the wave
805 (Godfrey and Moore, 1986), and appears to be the location of a dark band near
806 45°N flanked by 5- μm bright regions in Fig. 1. The northward gradient of poten-
807 tial vorticity (PV) was found to change sign at 44°N near to this jet, potentially
808 violating the stability criterion of Arnol'd's second theorem (Read et al., 2009)
809 and suggesting that the eddy activity (and possibly the enhanced NH_3 detected
810 by VIMS) arises due to instabilities in the flow at depth. If the two hemispheres

811 are symmetric at depth, we might expect a similar NH_3 enhancement at southern
812 mid-latitudes (44-51°S), and indeed Cassini imaging shows wave-like activity and
813 an abundance of small vortices at this latitude (Vasavada et al., 2006; Choi et al.,
814 2009). Unfortunately, these southern latitudes were not covered by the nightside
815 VIMS spectra studied here.

816 The band at 23-25°S, which is embedded in the region of prograde flow asso-
817 ciated with the equatorial jet, is also associated with a dark band in Fig. 1. The
818 upwelling band is poleward of the warm South Equatorial Belt (SEB) at 14-17°S,
819 and further north than Saturn's 'storm alley' (a region between 33-40°S charac-
820 terised by an abundance of vortices, Vasavada et al., 2006), but may be associ-
821 ated with wave-like activity and tilted streaks observed in the same latitude band
822 (Vasavada et al., 2006; Choi et al., 2009). Finally, despite these three regions of
823 upwelling, we cannot unambiguously identify the sink regions of gaseous NH_3 re-
824 quired for continuity. However, depletion of gaseous NH_3 could be provided by (i)
825 subsidence in regions flanking the upwelling, (ii) condensation to form fresh NH_3
826 clouds and (iii) photolysis to form hydrazine (a possible constituent of Saturn's
827 tropospheric hazes).

828 Aside from these three regions of upwelling, the NH_3 abundance is reason-
829 ably uniform, varying between 120-180 ppm in the northern hemisphere, and
830 slightly larger (120-220 ppm) in the south, depending on the scattering assump-
831 tions. Given the range of the results in Fig. 11, the NH_3 mole fraction derived
832 from VIMS is uncertain by a factor of 2. For the best fitting cloud models we
833 find globally-averaged abundances of 140 ± 50 ppm (scattering) and 200 ± 80
834 ppm (non-scattering) in the 1-4 bar sensitivity range of Fig. 6. The retrieved NH_3
835 abundance can be compared to the partial pressure for 100% relative humidity to

836 estimate the condensation altitudes for the gas. Equatorial NH_3 (500 ppm) would
837 condense near 1.65 bar, whereas the global mean abundance (140 ppm) suggests
838 condensation at 1.35 bar. This implies that NH_3 is saturated and well-mixed by
839 diffusive processes up to the 1.35-1.65 bar level (consistent with the expected
840 altitude of NH_3 condensation, Atreya et al., 1999), and then declines following
841 a saturated vapour-pressure curve and photolysis at lower pressures. Compared
842 to some of the previous disk-averaged NH_3 determinations in Table 1, we find
843 consistency with the 70-120 ppm values of Briggs and Sackett (1989), Grossman
844 et al. (1989), de Graauw et al. (1997, quoted for the 1.2-bar level), Orton et al.
845 (2000) and Burgdorf et al. (2004). The VIMS result is within the range of 50-200
846 ppm measured by Voyager/IRIS (Courtin et al., 1984) and slightly smaller than
847 the 500 ppm abundance at $p > 3$ bar derived from microwave spectra (de Pater
848 and Massie, 1985), except in the region of strong upwelling at the equator.

849 5.2.3. Arsenic

850 AsH_3 is the principal arsenic-bearing gas on Jupiter and Saturn, though pre-
851 vious studies have focussed solely on globally-averaged values. The meridional
852 distribution of AsH_3 is shown in Fig. 14j for the first time. Both scattering and
853 non-scattering cases indicate local maxima flanking the equatorial region, centred
854 on 7°N and 7°S . The two maxima are much closer to the equator than the warm
855 tropospheric belts ($\pm 15^\circ$) observed by CIRS (Fletcher et al., 2007b). However, the
856 non-scattering case predicts an AsH_3 asymmetry (from around 4 ppb in the south
857 to 2.5-3.0 ppb in the north) that is not apparent in the scattering case (uniform
858 abundance of 2.2 ± 0.3 ppb in both hemispheres). The global mean abundances
859 of AsH_3 in the scattering (2.2 ± 0.3 ppb) and non-scattering (3.3 ± 0.8 ppb) cases
860 are consistent with ground-based measurements of 3.0 ± 1.0 ppb (Noll and Larson,

861 1990) and $2.4_{-1.2}^{+1.4}$ ppb (Bézard et al., 1989), although VIMS spectra do not have the
862 spectral resolution to confirm the decreasing abundance with altitude (presumably
863 due to photolysis) detected by Bézard et al. (1989).

864 Like PH_3 , AsH_3 can be thought of as a tracer of tropospheric mixing, as
865 its abundance at the altitudes studied by VIMS greatly exceeds thermochemi-
866 cal equilibrium predictions (e.g., Fegley and Lewis, 1979; Fegley and Lodders,
867 1994). This disequilibrium is thought to be caused by vertical transport, mixing
868 parcels of air from the deep troposphere at a faster rate than AsH_3 can be chemi-
869 cally destroyed (conversion to solid phase As_4 or As_2S_2), thus the tropospheric
870 AsH_3 abundance represents Saturn's equilibrium composition at much deeper lev-
871 els (temperatures exceeding 400 K, Fegley and Lodders, 1994). Using the so-
872 lar photospheric composition of Grevesse et al. (2007), we estimate a supersolar
873 As/H ratio of 6.4-9.6 times solar (depending on the scattering and non-scattering
874 assumptions), larger than the subsolar ($0.6\times$) abundance on Jupiter (Noll et al.,
875 1990), whereas P/H is supersolar on both planets (Fletcher et al., 2009a). As
876 pointed out by Fegley and Lodders (1994), this difference is hard to explain be-
877 cause P and As exhibit similar cosmochemical behaviours, so we might expect
878 equal enrichments of both elements during accretion.

879 **6. Discussion: Possible Dynamical Mechanisms**

880 While detailed dynamical modelling is deferred to future studies, here we dis-
881 cuss some plausible speculations concerning the dynamical processes responsible
882 for the retrieved gaseous abundances and cloud distributions in Section 5. Fig.
883 14 indicated that the best-fitting VIMS models produce deep PH_3 ($p > 1.3$ bar)
884 and AsH_3 distributions that do not show the same meridional variations as NH_3

885 and high-altitude PH_3 ($p < 1.3$ bar). In particular, deep PH_3 and AsH_3 showed
886 local maxima either side of the equator, whereas the PH_3 scale height, the upper
887 cloud opacity and NH_3 show maxima directly at the equator. At first glance this is
888 difficult to interpret in terms of vertical transport from the deep troposphere, but
889 the two different regimes may be reconciled if we consider a scenario where two
890 stacked meridional circulation cells exist in Saturn's troposphere (see descriptions
891 by, Del Genio et al., 2009; Ingersoll et al., 2000; Showman and de Pater, 2005).

892 Cloud-tracking observations of eddy-momentum convergence on both Jupiter
893 and Saturn have long indicated that eddies accelerate the jets at pressures of 1
894 bar or deeper (Ingersoll et al., 1981; Salyk et al., 2006; Del Genio et al., 2007).
895 In steady state, these eddy accelerations would be balanced by meridional flow
896 that is equatorward across eastward jets and poleward across westward jets. This
897 meridional flow also helped to explain the prevalence of thunderstorms in jovian
898 belts (Gierasch et al., 2000; Ingersoll et al., 2000) and the distribution of NH_3 from
899 radio observations (e.g., Fig. 3 of Showman and de Pater, 2005). However, these
900 observations need to be reconciled with the 'classical' view of of the belt/zone cir-
901 culation on giant planets, whereby air rises in low-temperature anticyclonic zones
902 on the equatorial flanks of eastward jets and sinks in warmer cyclonic belts (e.g.,
903 Hess and Panofsky, 1951). The resulting meridional circulation causes poleward
904 motion across eastward jets and equatorward motion across westward jets, oppos-
905 ing the flow suggested by the jet-pumping scenario described above. In steady
906 state, the zonal Coriolis accelerations implied by this 'upper cell' circulation are
907 balanced by an unidentified source of atmospheric 'drag' that decelerates the jets
908 in the upper troposphere (Conrath and Pirraglia, 1983; Gierasch et al., 1986; Con-
909 rath et al., 1990).

910 The VIMS results require both the jet-pumping and the jet-damping circu-
911 lation regimes to be invoked (the stacked-cell hypothesis). In this scenario, we
912 suggest that drag within 20-30° of the equator enables a ‘classical’ meridional cir-
913 culation in the upper cell. Air rises and diverges (cools) within the equatorial zone,
914 advecting PH₃- and NH₃-rich air (along with aerosols to act as cloud nucleation
915 sites) from depths below the NH₃ cloud into the upper troposphere to explain the
916 equatorial maxima in Figs. 14c, g and i. This upper-cell air then moves poleward
917 to 10-20°, where it descends and warms over the equatorial belts, leading to the
918 relatively PH₃- and NH₃-depleted air at those latitudes. However, this classical
919 upper-cell circulation must give way in the deeper troposphere to a circulation
920 in the opposite sense. VIMS observations of off-equatorial maxima ($\approx \pm 10^\circ$) in
921 AsH₃ and deep PH₃ (Figs. 14h and j) suggest that air rises in the belts at 10-20°,
922 moves equatorward and descends at the equator.

923 While we stress that the stacked-cell hypothesis may not be a unique explana-
924 tion (and further predictive modelling is required), we note that these two different
925 circulation regimes emerge quite naturally from considerations of momentum bal-
926 ance of the jets - the jet-pumping eddies on Jupiter and Saturn likely result from
927 baroclinic instabilities or moist convection in the adiabatic region of the deep tro-
928 posphere. However, convection and instabilities are largely inhibited in the stably-
929 stratified upper troposphere so that eddies are confined to the deeper cell, leading
930 to jet damping (and the opposite sense of meridional circulation) in the upper cell.
931 The transition between the regimes of differing eddy behaviour (jet-pumping to
932 jet-damping) may be set by the thermal stratification of the atmosphere, which
933 grows larger in the upper troposphere. Numerical models of jet formation on the
934 giant planets indeed show deep circulation cells whose tops close at 1 bar, al-

935 though they do not consistently capture the hypothesized upper cells and the jet
936 decay with altitude, perhaps because the appropriate small-scale drag processes
937 in the upper troposphere (e.g., absorption of small-scale gravity waves) are not
938 represented (Lian and Showman, 2008). The mean circulation of the stacked cells
939 would not be closed systems, as turbulent small-scale eddy transport would permit
940 mixing of gases (e.g., mean flux of PH_3 , NH_3 and AsH_3) and aerosols vertically
941 between the cells, as well as creating temporal variability on the cell structure it-
942 self. Furthermore, the PH_3 and AsH_3 off-equatorial maxima have no counterparts
943 in the zonal jet structure (which shows a broad prograde jet at the equator), but
944 small-scale variations in the jet velocity (e.g., those recently detected by García-
945 Melendo et al., 2010) may produce localised vorticity-mixing barriers that could
946 be correlated with the distinct, narrow cloud lanes.

947 A second plausible explanation for the VIMS results involves eddy mixing,
948 which could play an important role in transport of heat and gaseous species as they
949 do on Earth (e.g., the Ferrel cell, where eddy heat transport dominates over mean
950 transport). The mean circulation would produce cold equatorial temperatures on
951 isobars in the upper cell (upwelling and divergence, as detected by Cassini/CIRS,
952 Fletcher et al., 2007b) and warm temperatures in the deep cell (convergence and
953 subsidence). A similar temperature pattern can also result from a single circula-
954 tion cell in the presence of latent heating warming the atmosphere at depth (e.g.,
955 Fig. 9 of Lian and Showman, 2010). Because the air is statically stable, isentropes
956 (surfaces of constant entropy) would bow upward at the equator in the upper cell
957 and downward in the lower cell (e.g., Fig. 5 of Showman and Ingersoll, 1998).
958 Mixing by eddy transport is almost isentropic on Saturn because of the long ra-
959 diative time constant. Hence eddy mixing in the upper cell transports NH_3 and

960 PH₃-laden air upward and equatorward from greater pressures (off the equator) to
961 lower pressures (at the equator). Similarly, eddy mixing in the deep cell would
962 transport PH₃ and AsH₃-poor air downward and equatorward from lower pres-
963 sures (off the equator) to greater pressures (at the equator). Thus quasi-isentropic
964 mixing by eddies could occur simultaneously with a mean non-isentropic merid-
965 ional flow (air crosses isentropes as it is heated and cooled), and both processes
966 are capable of explaining the meridional distributions of PH₃, AsH₃ and NH₃ ob-
967 served by VIMS.

968 Unfortunately, the spectral resolution of the VIMS data is too low to permit
969 full 2D (i.e., latitude and altitude) retrievals of PH₃, AsH₃ and NH₃ which would
970 allow further study of these different regimes. Furthermore, Section 4 indicated
971 that the separation of gaseous composition and aerosol scattering/absorption is
972 certainly non-unique. Although sensitivity extends over the 1-4 bar range in Fig.
973 6, we can obtain only a single 1D (i.e., latitudinal) estimate for AsH₃ and NH₃
974 abundances. Although the 1D distributions of these gases are consistent with the
975 stacked-cell hypothesis, 2D distributions from high spectral-resolution mapping
976 of these dynamical tracers is required to make advances in this field. However,
977 this hypothesis may also explain why visible reflectivity (which exhibits albedo
978 contrasts characteristic of the upper-cell meridional circulation in the jet-damping
979 region) appears so different from Saturn's 5- μ m appearance in Fig. 1 (representing
980 the jet pumping in the deeper meridional cell).

981 **7. Conclusions**

982 Cassini/VIMS maps of Saturn's 4.6-5.1 μ m nightside thermal emission have
983 been used to study the latitudinal distribution of opacity sources in Saturn's tro-

984 posphere between 38°S and 67°N (planetocentric). The spatial variation of at-
985 mospheric composition (PH₃, NH₃ and AsH₃) and aerosol properties (the opac-
986 ities of a compact 2.5-2.8 bar cloud and aerosols at $p < 1.4$ bar) are used to
987 probe the vertical dynamics and chemistry in the NH₃ and NH₄SH ice cloud-
988 forming regions of Saturn's troposphere. The spatial variability of Saturn's NH₃
989 and AsH₃ have been measured for the first time. Although the parameterisation
990 of the aerosol model (scattering versus non-scattering; compact versus extended
991 clouds; size distribution and refractive indices) has a significant effect on the re-
992 trieved opacities and gaseous abundances, we find that relative spatial variability
993 can be retrieved reliably from the VIMS spectra even if absolute abundances re-
994 main uncertain. This study provides the following conclusions:

- 995 1. **VIMS Sensitivity:** Maps of Saturn's thermal emission at 4.6-5.1 μm re-
996 veal a previously unseen dynamical regime in the adiabatic region of the
997 troposphere, with numerous narrow lanes of opacity variations (particularly
998 the dark lane $\pm 5^\circ$ of the equator); a strong mid-latitude seasonal asymme-
999 try in emission between $\pm 5^\circ - \pm 32^\circ$; and a plethora of discrete cloud fea-
1000 tures. This deep regime may be the region of eddy convergence which sup-
1001 plies momentum to the prograde jets (e.g., Del Genio et al., 2009), below
1002 the jet-drag region of the thermally-stratified upper troposphere. However,
1003 VIMS spectra are also sensitive to upper tropospheric clouds/hazes, with
1004 a seasonally-generated asymmetry in opacity attenuating the thermal emis-
1005 sion. Extensive testing of the retrieval model indicated VIMS sensitivity
1006 to both atmospheric composition (parameterised PH₃, well-mixed NH₃ and
1007 AsH₃, but not GeH₄, CO, H₂O or CH₄) and cloud properties.
- 1008 2. **Saturn's Clouds:** Spectral fitting was consistent with cloud opacity in two

1009 regimes - (i) a compact, meridionally-uniform cloud deck centred in the 2.5-
1010 2.8 bar region with small-scale opacity variations (20-30% at the resolution
1011 of the VIMS images used in this study) responsible for the narrow, bright
1012 axisymmetric lanes in VIMS images; and (ii) a hemispherically asymmetric
1013 upper cloud above the 1.4-bar level, whose exact altitude and vertical struc-
1014 ture are not constrained by VIMS, but which is likely to extend towards the
1015 tropopause and is responsible for reflected sunlight scattering on the day-
1016 side. The upper cloud shows a 1.5-2.0 times enhanced opacity within $\pm 10^\circ$
1017 of the equator. A scheme with a single-cloud layer was indistinguishable
1018 from the 2-cloud scheme at northern mid-latitudes, where the opacity of the
1019 upper cloud is at its smallest. The deep cloud base is poorly constrained in
1020 the southern hemisphere (it must exist at $p > 2$ bar) where the opacity of the
1021 upper cloud is at its largest. The meridional opacity distribution is highly
1022 sensitive to the optical properties of the clouds, but of the limited range of
1023 cloud compositions tested here, the optical constants of NH_4SH provided
1024 the best fits to the VIMS spectra. The deep cloud is not likely to consist
1025 of pure NH_3 ice, but more complex cloud compositions (e.g., a mixture of
1026 NH_3 and NH_4SH ; or the presence of P_2H_4 and other contaminants) cannot
1027 be ruled out. The 2.5-2.8 bar cloud is deeper than the predicted condensa-
1028 tion altitude of NH_3 (1.81 bar for a $5\times$ enrichment of heavy elements, Atreya
1029 et al., 1999) and higher than the predicted levels for NH_4SH condensation
1030 (5.72 bar), so its composition cannot be identified unambiguously.

1031 3. **Phosphine:** PH_3 dominates the morphology of the $5\text{-}\mu\text{m}$ spectrum, but its
1032 meridional variation is highly sensitive to the choice of cloud model. A
1033 well-mixed PH_3 distribution failed to reproduce the spectrum, and we found

1034 that the abundance begins to decline for $p < 1.3$ bar (lower pressures at
1035 the equator). The fractional scale height for the upper-tropospheric PH_3
1036 generally showed a maximum at the equator and a mid-latitude asymme-
1037 try (consistent with the results from Cassini/CIRS, Fletcher et al., 2009a).
1038 The deep PH_3 showed an equatorial minimum flanked by two off-equatorial
1039 maxima ($\pm 10^\circ$). However, deep mole fractions in the scattering (mean and
1040 standard error 3.1 ± 0.3 ppm) and non-scattering (4.4 ± 0.6 ppm) cases were
1041 smaller than the 6.4 ± 0.4 ppm mole fraction reported by CIRS, and the
1042 $p_0 = 1.3$ -bar transition from the well-mixed to the photolysis region was
1043 much deeper than that derived from CIRS ($p_0 = 0.55$ bar). Uncertainties
1044 in the cloud spectral properties, as well as the PH_3 line data, are the likely
1045 source of this CIRS-VIMS discrepancy, requiring joint modelling to resolve
1046 this issue.

- 1047 4. **Ammonia:** NH_3 has a significant effect on the spectrum near $5.1 \mu\text{m}$ and a
1048 similar spatial distribution for all cloud models tested, being elevated within
1049 $\pm 5^\circ$ of the equator (in a region of strong $5\text{-}\mu\text{m}$ attenuation) by three times
1050 the northern mid-latitude abundances. Extratropical upwelling is also sug-
1051 gested by small enhancements at $23\text{-}25^\circ\text{S}$ and $42\text{-}47^\circ\text{N}$. The northern peak
1052 is associated with a $5\text{-}\mu\text{m}$ dark band just north of the prograde jet at 41°N ,
1053 and may be associated with abundant eddy activity and the ‘ribbon wave’
1054 at this latitude. Aside from the three regions of upwelling, the NH_3 abun-
1055 dance was latitudinally uniform, with globally averaged 1-3 bar abundances
1056 of 140 ± 50 ppm (scattering) and 200 ± 80 ppm (non-scattering), rising to
1057 300-500 ppm at the equator.
- 1058 5. **Arsine:** The spatial variability of Saturn’s principal arsenic-bearing gas has

1059 been measured for the first time, showing local maxima at $\pm 7^\circ$ and a mini-
1060 mum at the equator. An AsH_3 asymmetry (from around 4 ppb in the south
1061 to 2.5-3.0 ppb in the north) was detected using non-scattering clouds, but
1062 is not apparent in the more physically-realistic scattering models (uniform
1063 abundance of 2.2 ± 0.3 ppb in both hemispheres). This results in a supersolar
1064 As/H ratio of 6.4-9.6 times solar, larger than the subsolar ($0.6\times$) abundance
1065 on Jupiter. This difference between the two gas giants is unexpected, as P/H
1066 is supersolar on both planets and the two species should have shared many
1067 common properties during planetary accretion.

1068 Exploitation of the $5\text{-}\mu\text{m}$ window by Cassini/VIMS has revealed a planet with
1069 symmetric dynamics at depth coupled to substantial seasonal asymmetries in the
1070 upper troposphere. However, uncertainties in the properties and distribution of
1071 Saturn's clouds produces significant degeneracies in modelling the VIMS data.
1072 Future work should focus on (a) comparing dayside $4.6\text{-}5.1\ \mu\text{m}$ spectra to those
1073 on the nightside to quantify the effects of sunlight scattering; (b) exploiting 1-
1074 $4\ \mu\text{m}$ reflection spectroscopy of Saturn's clouds to constrain the vertical aerosol
1075 distribution and phase function; (c) incorporating new constraints on aerosol size
1076 distributions and optical properties to constrain gaseous retrievals; and (d) produc-
1077 ing regional maps of isolated dynamic features to qualitatively assess the physical
1078 reality of the retrieval model. Future near-infrared instruments for giant planet
1079 exploration should feature improved spectral resolutions in the $5\text{-}\mu\text{m}$ window
1080 to break the degeneracies between aerosols and composition and permit fully
1081 3-dimensional retrievals to trace tropospheric dynamics within and beneath the
1082 condensation clouds.

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1093 **Figure Captions**

1094 **Figure 1:** Four examples of the VIMS-IR radiances at (a) 5.1; (b) 5.0; (c) 4.8
1095 and (d) 4.6 μm . Radiances from eight cubes in Table 2 were reprojected onto a
1096 cylindrical map, selecting only regions that were well separated from the day/night
1097 terminator. No attempt has been made to correct for the motion of cloud features
1098 due to the zonal flow (see main text), resulting in some apparent disconnect at
1099 the overlap points. We have not corrected for limb darkening in these images,
1100 resulting in the visible seams where the cubes overlap. Thermal emission was
1101 obscured by the noise at wavelengths shorter than 4.5 μm .

1102 **Figure 2:** Comparisons of zonally-averaged radiances (a) and brightness
1103 temperatures (b) for five latitudes (the equator, ± 15 and $\pm 30^\circ$) extracted from the
1104 image cubes in Fig. 1. Prominent features in the spectrum are labelled in panel (b)
1105 in their approximate locations, but these gases actually have effects over a wider
1106 region of the low-resolution VIMS spectrum than indicated here. Radiance errors
1107 described in the main text are indicated in panel (a).

1108 **Figure 3:** Optical constants for the range of cloud compositions considered
1109 in this study (a key for the different lines is shown in (b). Imaginary (a) and
1110 real (b) refractive indices are taken from the listed references. Extinction cross-
1111 sections (c) and single scattering albedoes (d) were calculated using Mie theory
1112 for a standard gamma distribution of particles of radius $r = 1.0 \pm 0.05 \mu\text{m}$. The
1113 key difference between the compositions is the enhanced absorption of NH_4SH -
1114 like species (Ferraro et al., 1980; Howett et al., 2007) between 4.7 and 4.9 μm .

1115 **Figure 4:** Variation of phase function with scattering angle for the range of
1116 cloud compositions used in this study. Phase functions were calculated as a two-
1117 term Henyey-Greenstein (HG) functions based on the optical properties listed in

1118 the key. With the exception of the isotropic scatterer, there is little to distinguish
1119 between these phase functions, which is mostly governed by the choice of particle
1120 sizes ($r = 1.0 \pm 0.05 \mu\text{m}$).

1121 **Figure 5:** Sensitivity of VIMS nightside spectra to a selection of gases in
1122 the model atmosphere. Spectra were calculated using a compact grey-absorbing
1123 cloud in the absence of scattering, with molecular abundances scaled from 0.1-10
1124 times the *a priori* values (key is shown in panel i). PH_3 , NH_3 and AsH_3 have the
1125 largest effects over this spectral range.

1126 **Figure 6:** Examples of the functional derivatives (Jacobians, the rate of
1127 change of radiance with a particular model parameter) for temperature and several
1128 gases contributing to the 5- μm window. Spectra were calculated using a compact
1129 grey-absorbing cloud (model II.A), so results will vary depending on the proper-
1130 ties of the absorbing gases. Jacobians have been normalised to unity for each gas,
1131 and this does not represent their relative contribution to the spectrum (see Fig. 5,
1132 for example). A scale bar is shown for the central three panels. VIMS spectra are
1133 mostly sensitive to compositional variations in the 1-3 bar region.

1134 **Figure 7:** Contribution function (product of the transmission weighting func-
1135 tion and the Planck black body function) calculated for a cloud-free case for the
1136 VIMS spectrum. The contribution function shows a maximum sensitivity to the
1137 5-bar level.

1138 **Figure 8:** Contours of χ^2 for VIMS retrievals varying the base pressure p_b of
1139 the deep cloud layer and the transitional pressure p_0 from well-mixed deep PH_3
1140 to PH_3 in the photochemical depletion region. Three representative latitudes are
1141 shown, indicating that the best fitting p_0 is 1.3 bar, although this can be at lower
1142 pressures at the equator.

1143 **Figure 9:** The meridional distribution of χ^2 for optical models A-C (grey,
 1144 NH_3 and NH_4SH cloud scattering properties), which depend on the scattering
 1145 processes (T=non-scattering, S=scattering) and vertical models (I-IV). These re-
 1146 trievals were performed for 22 coarsely gridded VIMS zonal mean spectra using
 1147 the grey-cloud approximation. Comparison of these values was used to rule out
 1148 certain optical models and vertical distributions, although considerable degenera-
 1149 cies still exist.

1150 **Figure 10:** Demonstration of the dependence of retrieved cloud optical
 1151 depths on the chosen aerosol models (T=non-scattering, S=scattering). Panels
 1152 (a) and (b) show the opacity of the deep cloud and the spurious emission angle de-
 1153 pendence when grey scatterers are assumed. Panel (c) shows that the north-south
 1154 asymmetry in upper-cloud opacity is present for all model assumptions. The cor-
 1155 responding χ^2 are shown in Fig. 9.

1156 **Figure 11:** Demonstration of the degeneracy in gaseous distributions of
 1157 NH_3 , AsH_3 and PH_3 depending on the choice of aerosol optical models (T=non-
 1158 scattering, S=scattering) and vertical models (I-IV). The corresponding χ^2 are
 1159 shown in Fig. 9.

1160 **Figure 12:** Trade off between the different atmospheric parameters for three
 1161 latitudes, 15°S (left column), the equator (central column) and 15°N (right col-
 1162 umn). The seven rows show (a) the variation of χ^2/N with base pressure, where
 1163 N is the number of spectral channels ($N = 32$, so a $\Delta\chi^2 = 1$ envelope corresponds
 1164 to 0.03 in these panels) in the retrieval; (b-c) the PH_3 deep mole fraction and
 1165 fractional scale height; (d-e) the opacity of the deep and upper clouds in model
 1166 II.A; (f-g) the well-mixed mole fractions of AsH_3 and NH_3 . The vertical dashed
 1167 line shows the best-fitting base pressure for each latitude (note that it is poorly

1168 constrained in the southern hemisphere case).

1169 **Figure 13:** Scatter plots showing positive correlations between synthetic
1170 VIMS spectral inputs ('true' values) and the retrieved outputs. The only figures
1171 showing no correlation is GeH₄, which cannot be reliably retrieved from the VIMS
1172 data. The deviation between true and retrieved parameters (the dotted line shows
1173 a 1:1 relationship) is used to define the random error on retrieved quantities.

1174 **Figure 14:** Meridional distributions of Saturn's cloud and aerosol properties
1175 (panels c-e) and gaseous distributions (panels g-j), for the two best-fitting cloud
1176 models: an upper haze and a deep compact cloud, with the non-scattering grey
1177 assumption (solid line, model A) and the scattering NH₄SH assumption (dotted
1178 line, model C). These are compared to the zonal mean radiances and brightness
1179 temperatures in panels a and f, respectively. Although the scattering model shows
1180 a small improvement in χ^2 in panel a, suggesting that the optical properties of
1181 NH₄SH produce the best results, this improvement is deemed insignificant given
1182 the degeneracies discussed in the main text. The points with error bars at 60°S
1183 show the formal retrieval uncertainty in each quantity.

1184 **Figure 15:** The best-fitting spectral models to five selected latitudes. Both
1185 the thermal non-scattering and NH₄SH scattering models (lines) produce near-
1186 identical fits to the data (individual points). Overfitting at 4.67 and 4.85 μm , and
1187 underfitting at 5.06 μm , are common features of all spectral models and could not
1188 be explained by the addition of further gaseous species.

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Reference	q_{NH_3}	Method
Courtin et al. (1984)	$(0.5 - 2.0) \times 10^{-4}$	Voyager/IRIS 180-300cm ⁻¹
de Pater and Massie (1985)	5×10^{-4} at $p > 3$ bar 3×10^{-5} at $p < 1.25$ bar	Very Large Array (VLA)
Briggs and Sackett (1989)	$0.7 - 1.1 \times 10^{-4}$ at $p = 2$ bar	radio T_B
Grossman et al. (1989)	1.2×10^{-4} around condensation level	VLA
Noll and Larson (1990)	Upper limit 3×10^{-4}	$5 \mu\text{m}$ spectra
de Graauw et al. (1997)	1.1×10^{-4} at $p = 1.2$ bar	ISO/SWS
Kerola et al. (1997)	Less than 1×10^{-9} at RC boundary	$3 \mu\text{m}$ data
Orton et al. (2000)	1×10^{-4} with 3-4 \times uncertainty	Sub-mm PH ₃ analysis
Burgdorf et al. (2004)	1×10^{-4}	ISO/LWS 96-101cm ⁻¹
Kim et al. (2006)	6×10^{-8} at 460 mbar 3×10^{-8} at 390 mbar	$3 \mu\text{m}$ data
Fletcher et al. (2009a)	$(3.3 \pm 0.3) \times 10^{-7}$ at 690 mbar	Cassini/CIRS Far-IR

Table 1: Vertical distribution of ammonia mole fraction from previous determinations.

Cube	Date	Start Time (UTC)	Stop Time (UTC)	Longitude	Range (km)	Phase (deg)
CM_1524383985	2006-Apr-22	07:29:22	08:04:01	128.1	2806258	114
CM_1524388848	2006-Apr-22	08:50:25	09:25:04	173.5	2793264	114
CM_1524393612	2006-Apr-22	10:09:49	10:44:28	218.1	2780503	114
CM_1524400806	2006-Apr-22	12:09:43	12:44:22	285.3	2760982	113
CM_1524403247	2006-Apr-22	12:50:24	13:25:03	308.1	2754393	113
CM_1524408018	2006-Apr-22	14:09:55	14:44:34	352.8	2741313	113
CM_1524412815	2006-Apr-22	15:29:52	16:04:31	37.6	2728032	113
CM_1524417617	2006-Apr-22	16:49:54	17:24:33	82.4	2714716	113

Table 2: VIMS-IR Cubes used in this study. The quoted longitude is for System III West at the start time of the observations.

Cloud Model	Description	Variables and Comments
I	Single Compact Cloud	p_b, τ_1
II	Two Compact Clouds	p_b, τ_1, τ_2 (Grey upper cloud fixed at 1.5 bar)
III	Single Extended Cloud	p_b, τ_1 (Extends to the tropopause)
IV	Compact Upper, Extended Deep	p_b, τ_1, τ_2 (Grey upper cloud fixed at 1.5 bar)
A	Grey cloud	Grey cross-section and $\omega_0 = 0.95$ across the full range; isotropic phase function
B	NH ₃ ice	Martonchik et al. (1984)
C	NH ₄ SH	Ferraro et al. (1980)
D	Modified pseudo-NH ₄ SH	Refractive index $2.3 + 0.01i$ Nixon et al. (2001)
E	Updated NH ₄ SH	Howett et al. (2007)

Table 3: Summary of cloud models tested in this study, vertical structures I-IV, optical models A-E.

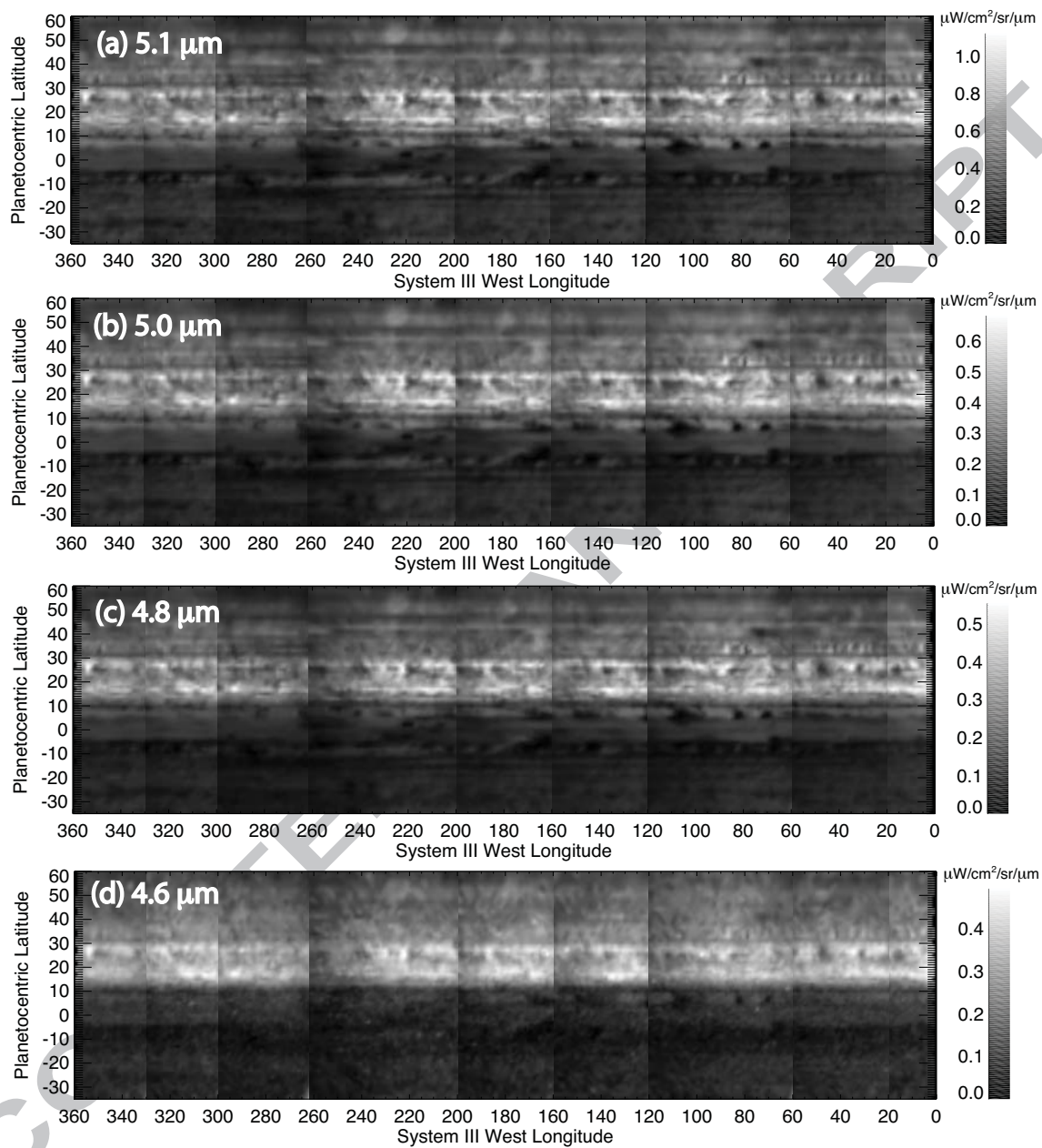


Figure 1:

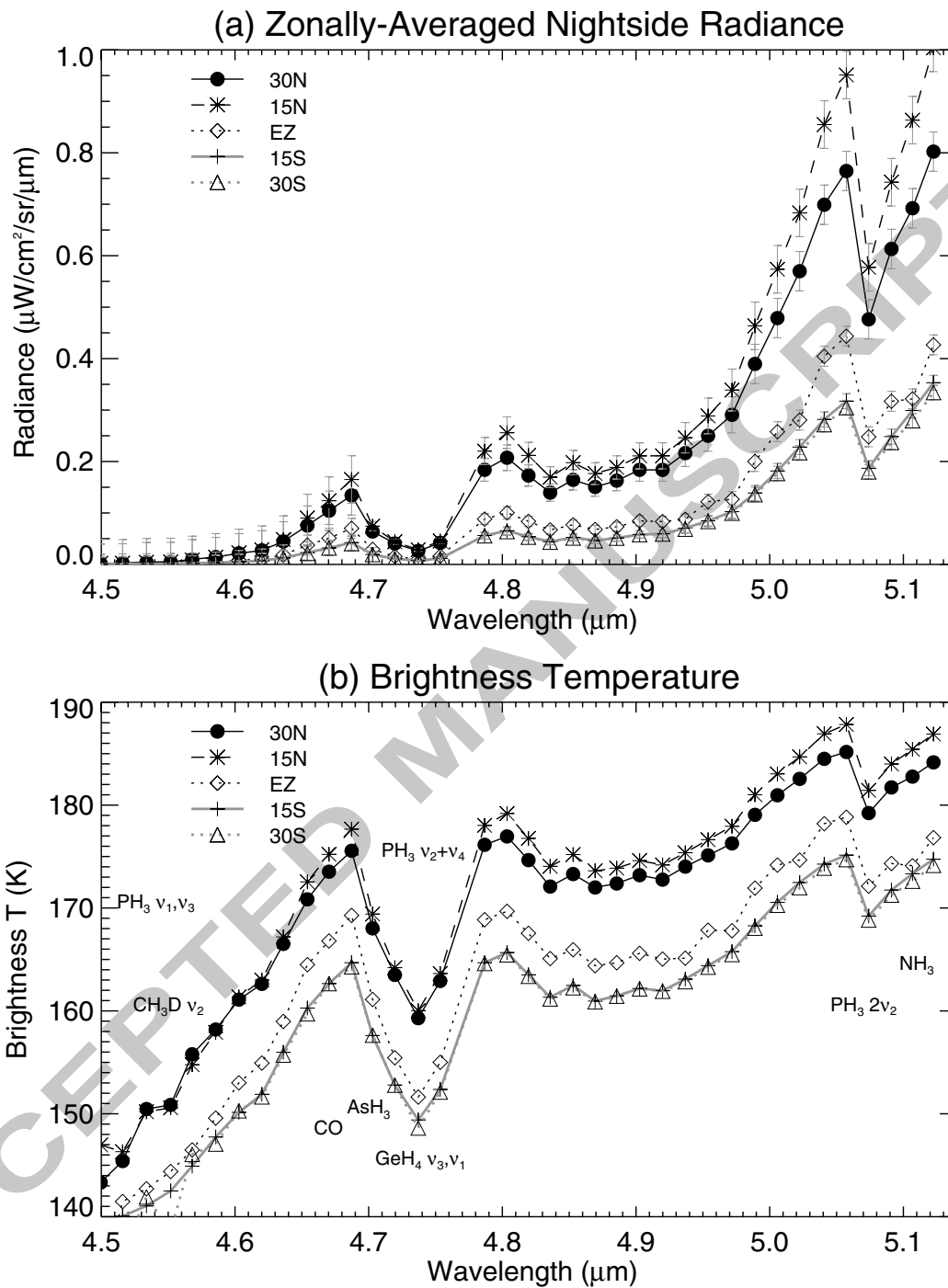


Figure 2:

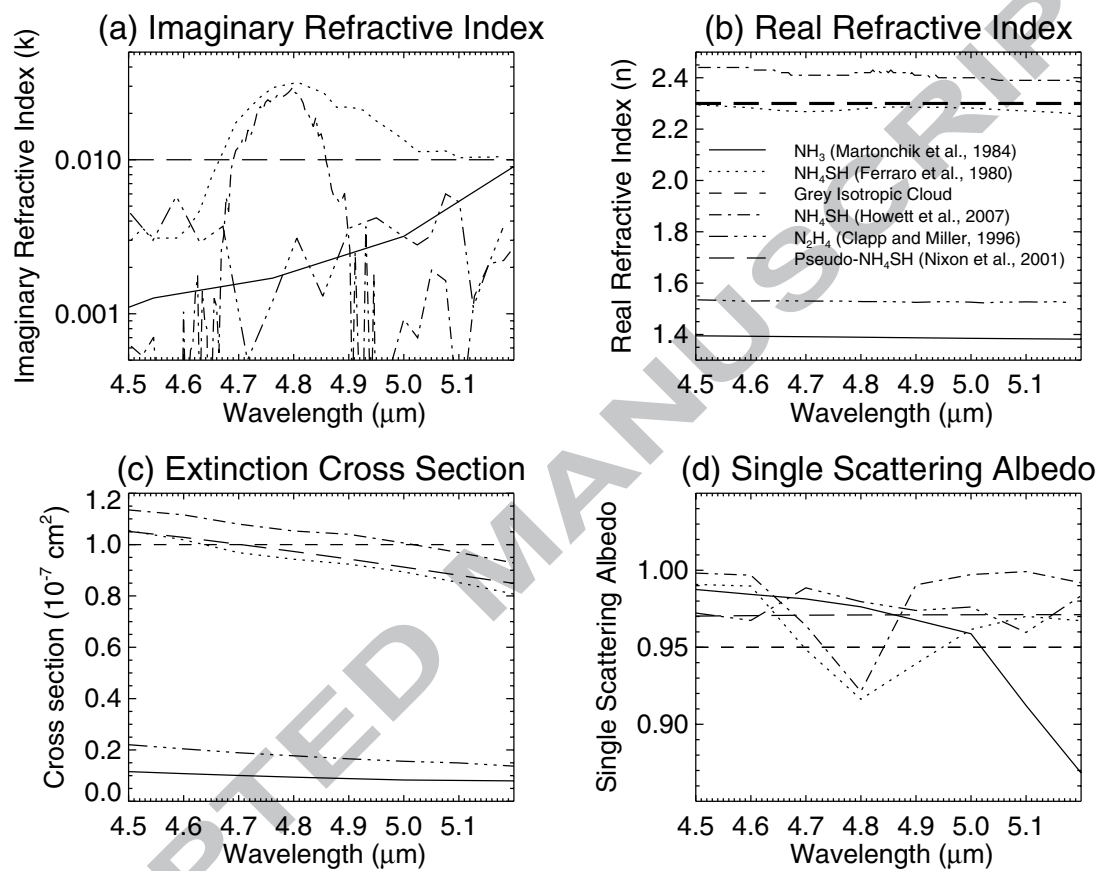


Figure 3:

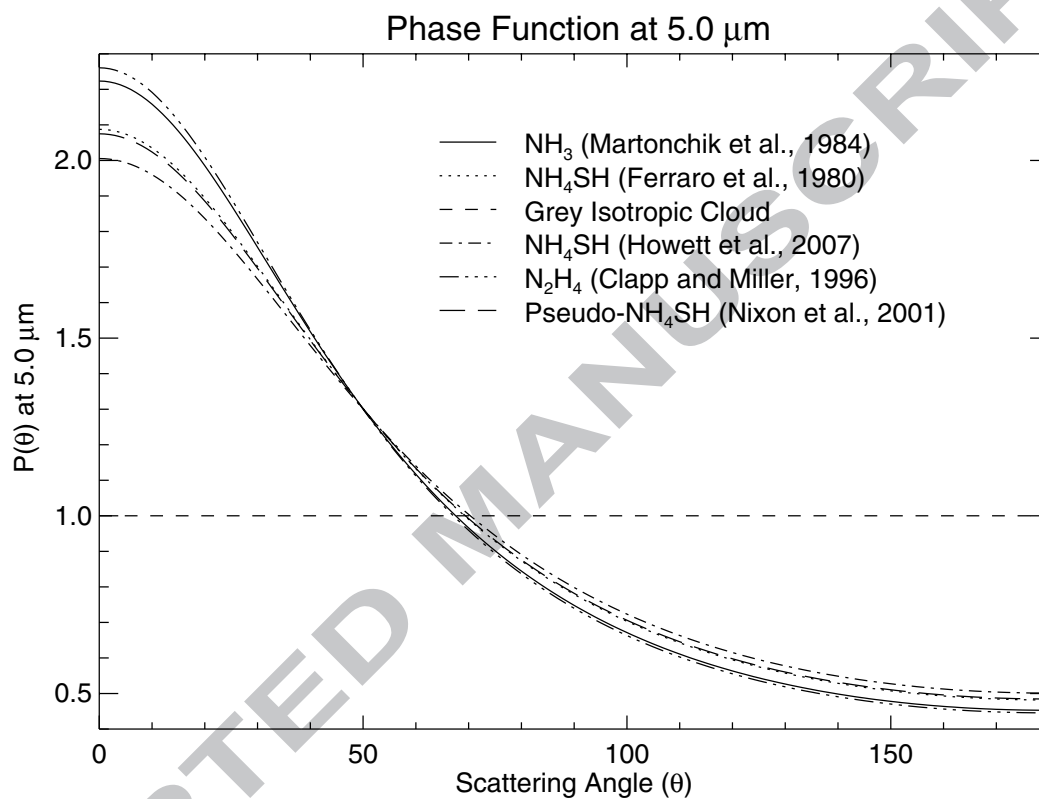


Figure 4:

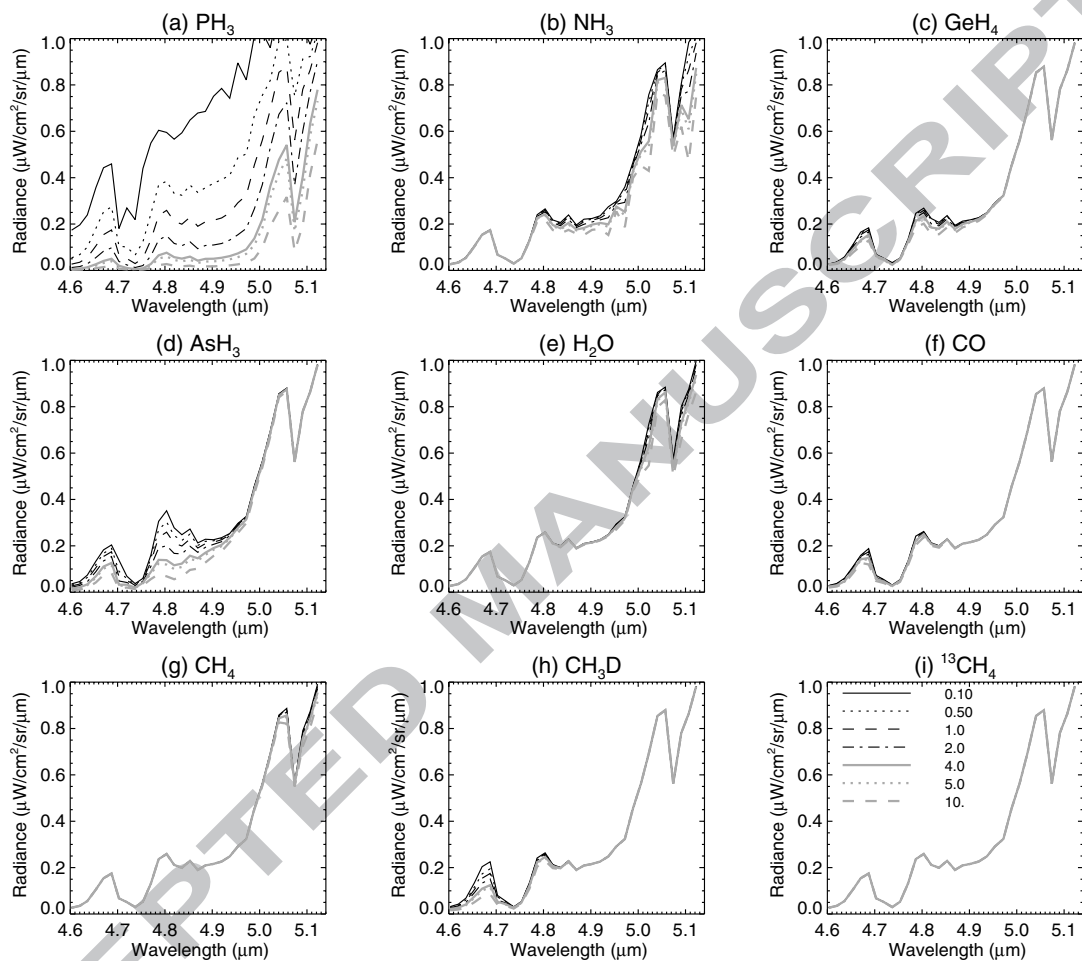


Figure 5:

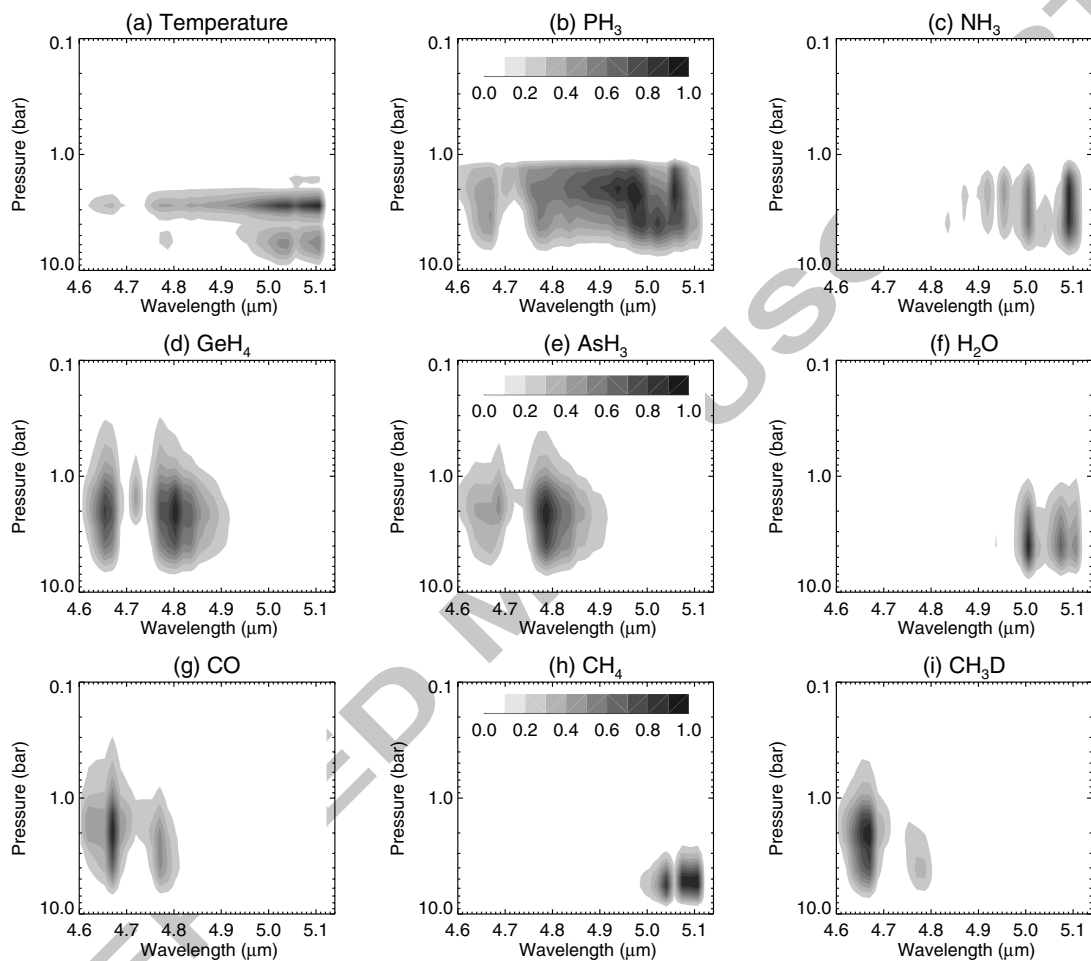


Figure 6:

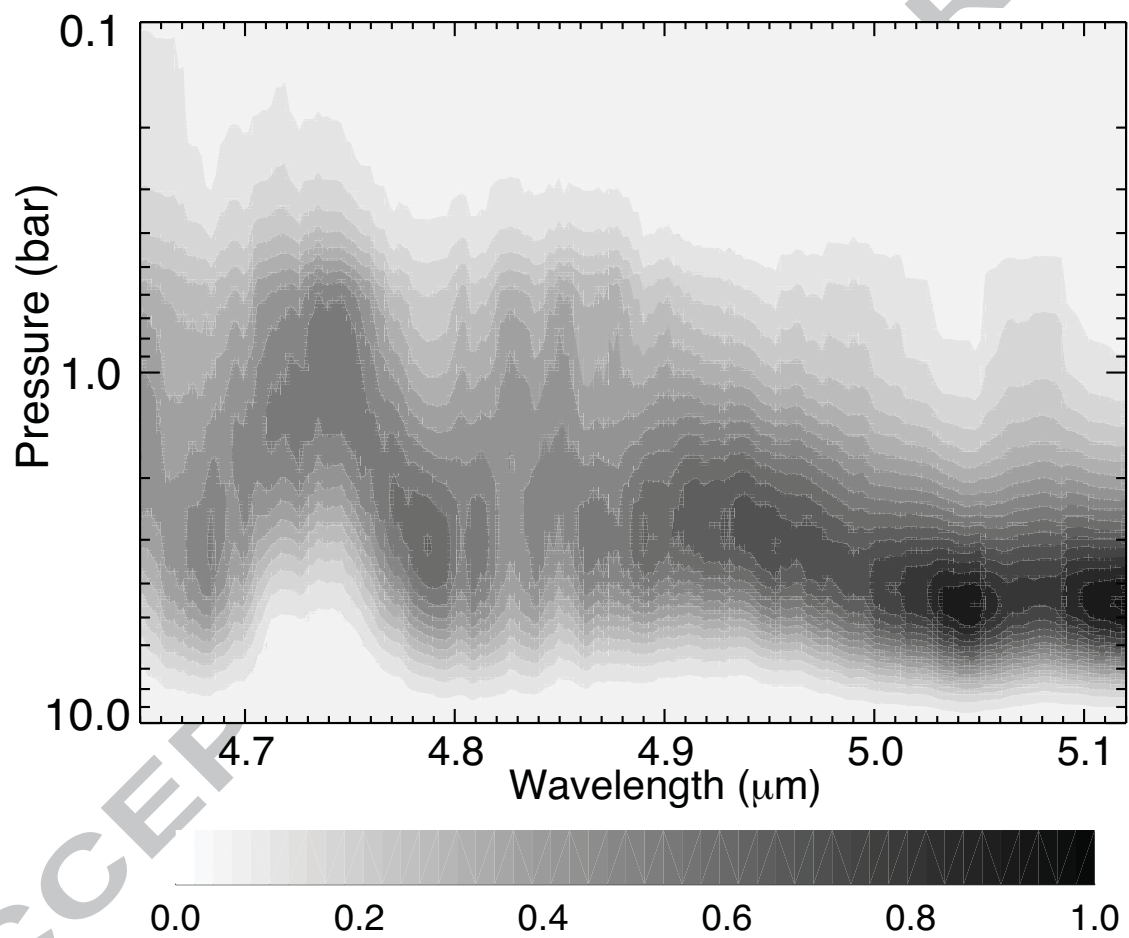


Figure 7:

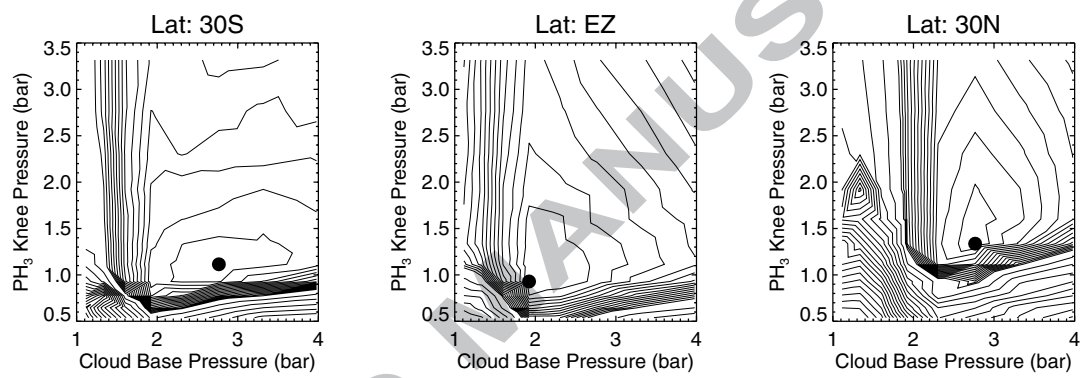


Figure 8:

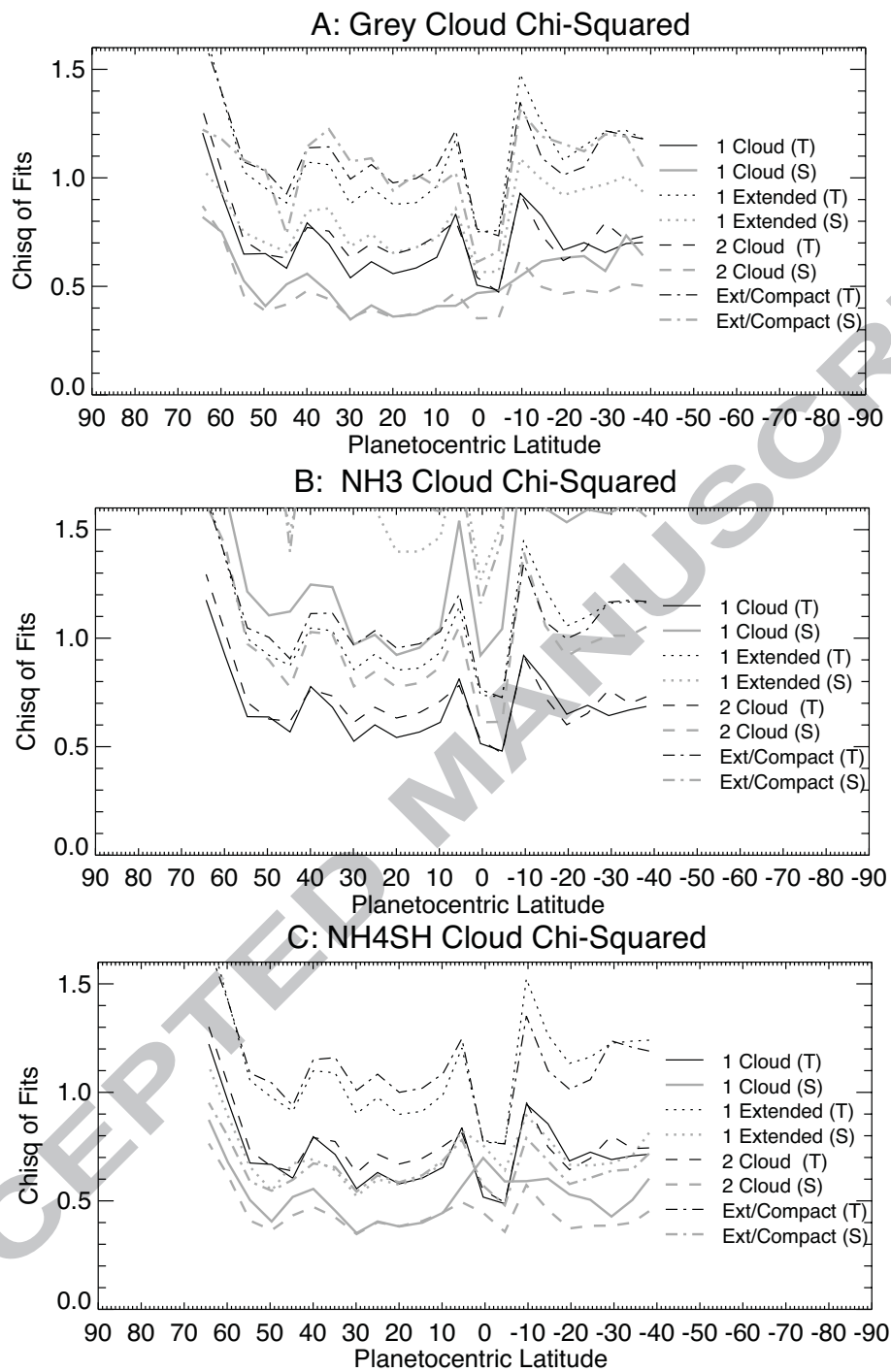


Figure 9:

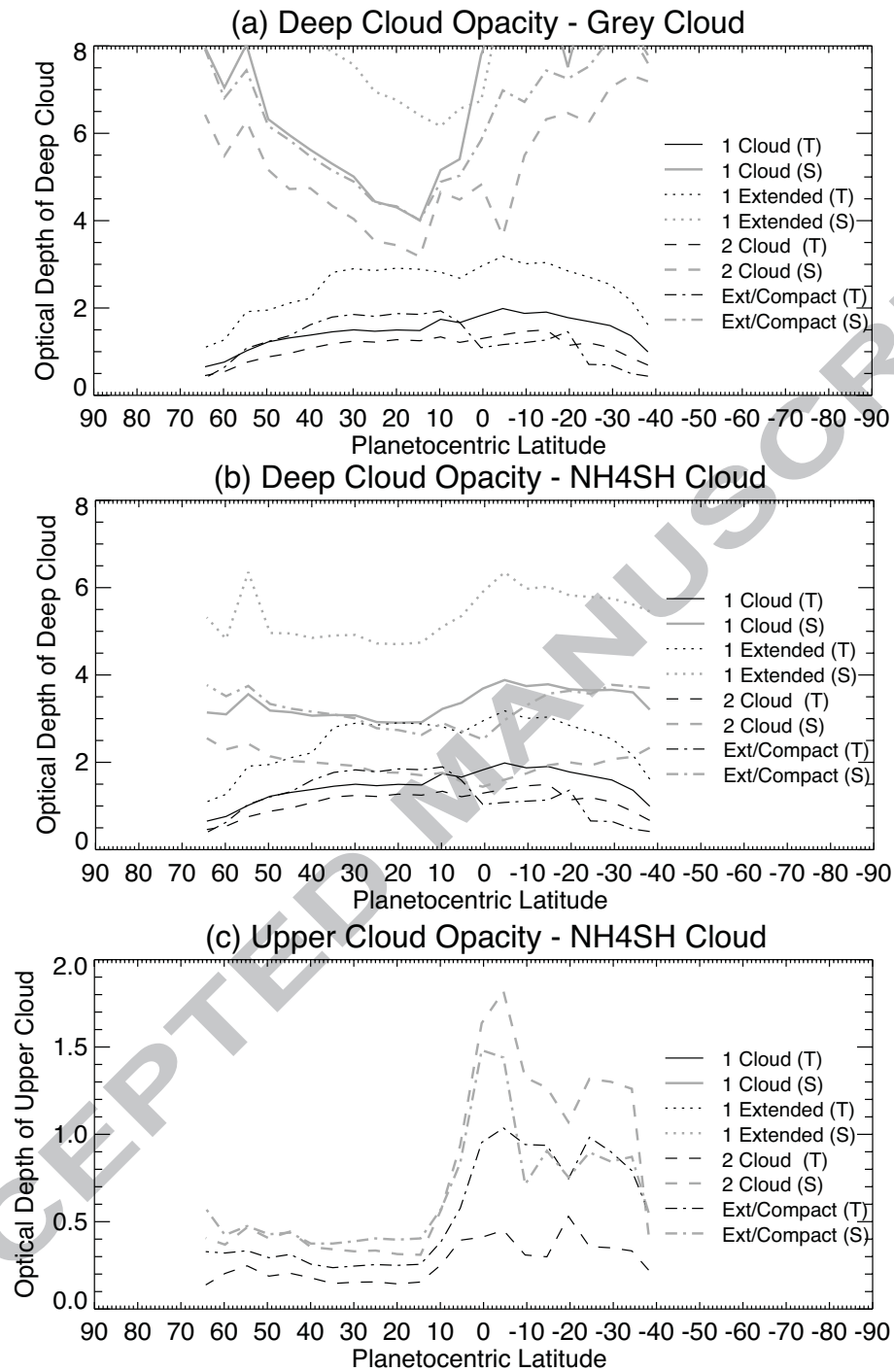


Figure 10:

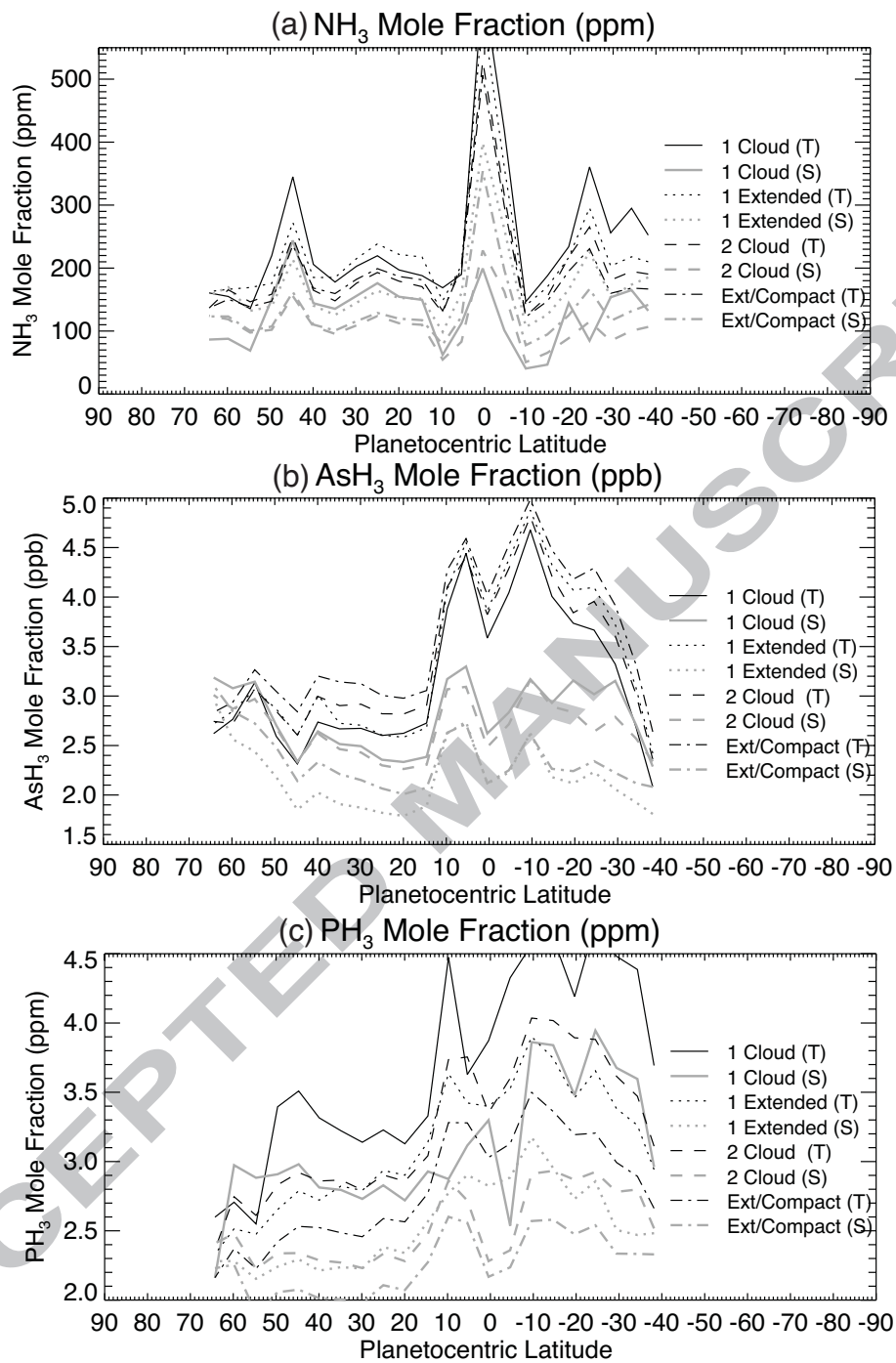


Figure 11:

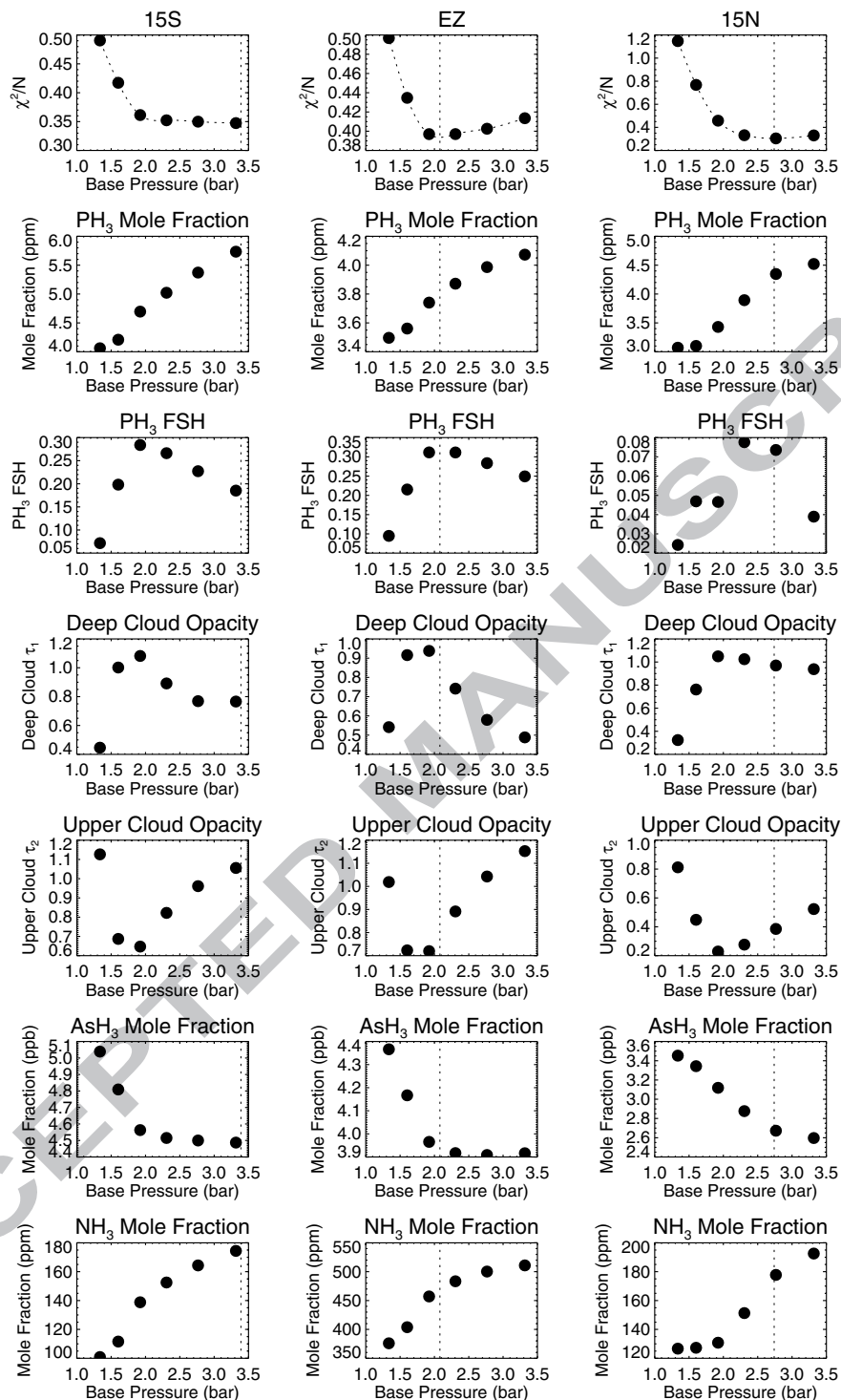


Figure 82:

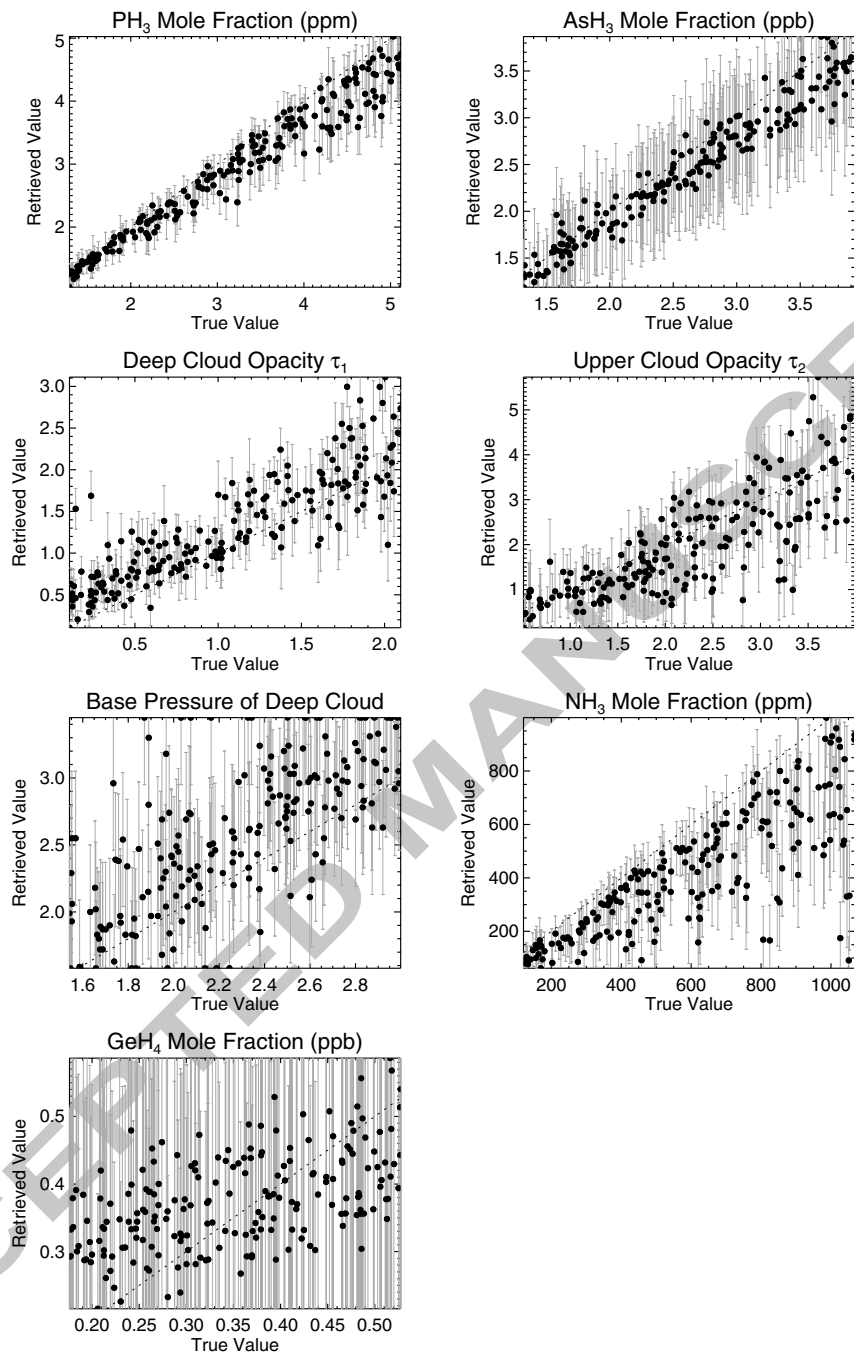


Figure 13:

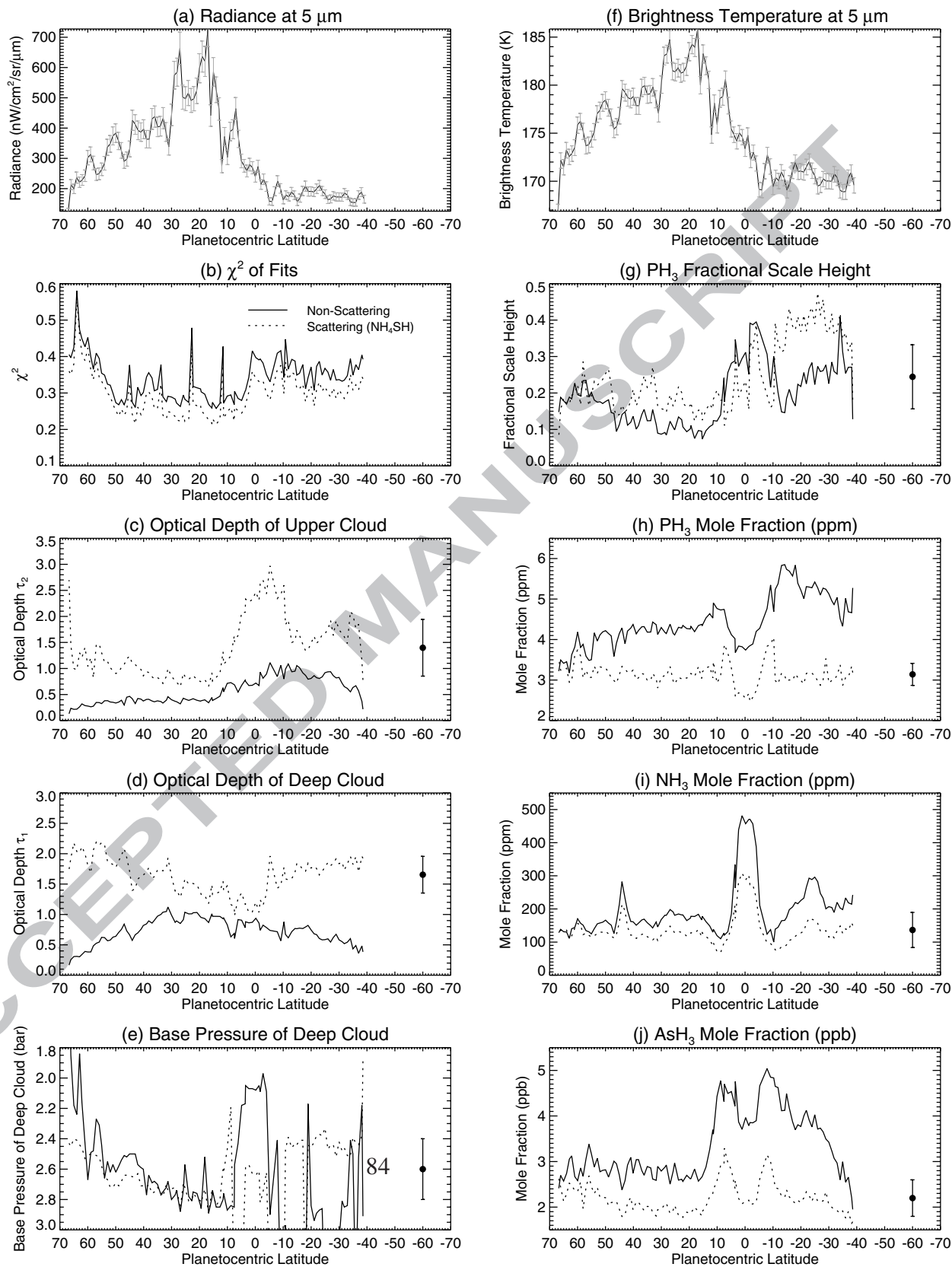


Figure 14:

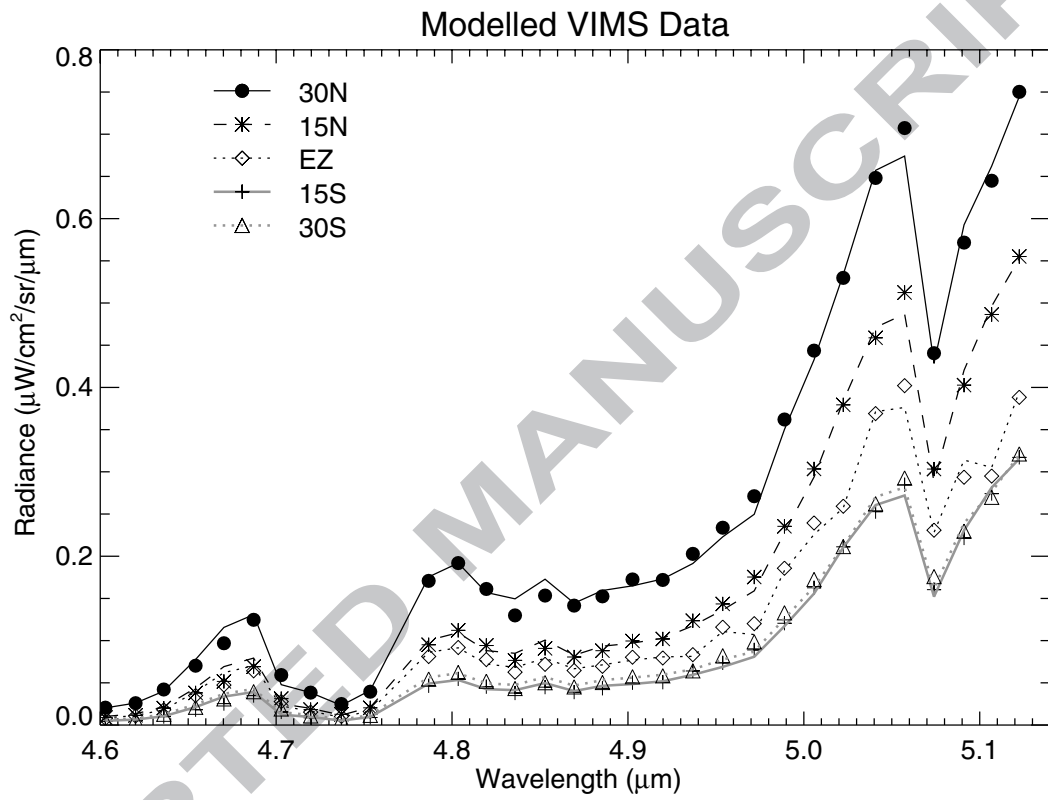


Figure 15:

Research Highlights***Saturn's Tropospheric Composition and Clouds from Cassini/VIMS 4.5-5.1 μm Nightside Spectroscopy******Fletcher et al.***

- Saturn's spectrum contains a low-opacity window allowing us to study the atmosphere beneath the tropospheric hazes.
- Upwelling dredges ammonia, aerosols and phosphine to high altitudes at Saturn's equator.
- Strong extra-tropical upwelling and storms occur in broad regions near jets at 41N and 25S.
- Saturn's upper tropospheric hazes vary seasonally, whereas deep clouds are more uniform.
- Gases and clouds measured at 5 μm can be used to trace the circulation of Saturn's deep atmosphere.