EVOLUTION OF SATURN’S NORTH POLAR COLOR AND CLOUD STRUCTURE BETWEEN 2012 AND 2017 INFERRED FROM CASSINI VIMS AND ISS OBSERVATIONS

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ABSTRACT

Cassini/ISS imagery and Cassini/VIMS spectral imaging observations from 0.35 to 5.12 μm show that Saturn’s north polar region (70° – 90°N) evolved significantly between 2012 and 2017, with the region poleward of the hexagon changing from dark blue/green to a more dramatically brighter gold color, except for the inner eye region (88.2° – 90°N), which remained relatively unchanged. These and even more dramatic near-IR changes can be reproduced by an aerosol model of four compact layers consisting of a stratospheric haze at an effective pressure near 50 mbar, a deeper haze of putative diphosphine particles typically near 300 mbar, an ammonia cloud layer with a base pressure between 0.4 bar and 1.3 bar, and a deeper cloud of a possible mix of NH₄SH and water ice particles within the 2.7 to 4.5 bar region. Between the eye and the hexagon boundary near 75°N were many small discrete bright cloud features that VIMS spectra indicate have increased opacity in the ammonia cloud layer. Our analysis of the background clouds between the discrete features shows that between 2013 and 2016 the effective pressures of most layers changed very little, except for the ammonia ice layer, which decreased from about 1 bar to 0.4 bar near the edge of the eye, but increased to 1 bar inside the eye. Inside the hexagon there were large increases in optical depth, by up to a factor of 10 near the eye for the putative diphosphine layer and by a factor of four over most of the hexagon interior. Inside the eye, aerosol optical depths were very low, suggesting downwelling motions. The high contrast between eye and surroundings in 2016 was due to substantial increases in optical depths outside the eye. The color change from blue/green to gold inside most of the hexagon region can be explained in our model almost entirely by changes in the stratospheric haze, which increased between 2013 and 2016 by a factor of four in optical depth and by almost a factor of three in the short-wavelength peak of its wavelength-dependent imaginary index. A plausible mechanism for increasing aerosol opacity with time is the action of photochemistry as the north polar region became increasingly exposed to solar UV radiation. For 2013 we found an ammonia mixing ratio of about 50×10⁻⁶ in the depleted region between 4 bars and the NH₃ condensation level (~ 1 bar), but the NH₃ results for 2016 are unclear due to very high retrieval uncertainties associated with increased aerosol opacity. We retrieved a deep abundance of about 5×10⁻⁶ for PH₃ and a pressure break point (where the PH₃ abundance begins to decline with altitude) that coincided with the main cloud top near 300 mbar, except when that cloud opacity was very low, at which point the PH₃ break point pressure generally increased substantially, consistent with prior suggestions that the cloud layers shield PH₃ from destruction by UV radiation above the clouds. We found an average AsH₃ mixing ratio of 2×10⁻⁹ with some evidence for a decline with altitude above the main cloud layer.

Subject headings: : Saturn; Saturn, Atmosphere; Saturn, Clouds

1. INTRODUCTION

The Cassini observations of Saturn’s atmosphere extended from 2004 until atmospheric entry on 15 September 2017. As illustrated in the plot of subsolar latitude versus time (Fig. 1), the mission extended over nearly a complete seasonal half-cycle, beginning just a few years after the October 2002 southern summer solstice and ending a few months after the May 2017 northern summer solstice. Both polar regions were found to be encircled by strong cyclonic vortex circulations (Orton and Yanamandra-Fisher 2005), with a visual similarity to hurricanes on earth, including dark eyes centered on the poles and, in the case of the southern vortex, what appeared to be eyewall clouds casting long shadows (Dyudina et al. 2008, 2009). However, a detailed radiative transfer analysis of the southern region did not find any deep convective wall clouds, but instead a region of generally low aerosol optical depth, with shadows cast by spatially sharp but small optical depth transitions in relatively translucent layers (Sromovsky et al. 2020a,b). Also found in the southern region were discrete bright features with 3-μm spectral signatures, characteristic of ammonia ice clouds, which are generally not visible on Saturn.
except in association with convective storm systems such as those in Storm Alley (Baines et al. 2009a; Sromovsky et al. 2018) or in the Great Storm of 2010-2011 (Sromovsky et al. 2013). The corresponding spectra of these south polar features were well modeled by locally increased optical depths in the ammonia cloud layer, which were visible in the polar region due to the small optical depth of the overlying haze layers (Sromovsky et al. 2020a).

The north polar region is remarkable not only for the existence of a hexagonal weather pattern associated with a meandering zonal jet (Sayanagi et al. 2019), but also for the remarkable color transformation that occurred within the hexagon as the planet approached northern summer solstice. As shown in press-release images reproduced in Fig. 2, the natural color of the region transformed from a blue/green color to an orange/gold color, a presumed result of solar UV photochemistry producing a haze of particles in the upper troposphere that began to resemble in color the top haze layer seen over most of the rest of Saturn. In spite of this upper haze layer, underlying discrete ammonia cloud features were also seen inside the hexagon, even when the haze was its thickest, near the end of the Cassini mission. This was demonstrated by an initial analysis of the 2017 high spatial resolution Grand Finale VIMS observations of the north polar region close to and within its eye (Baines et al. 2018). Besides finding evidence for local convection associated with discrete ammonia clouds, they also found generally very low optical depths, especially within the eye region, which did not undergo the color transformation seen in the rest of the polar region, and where aerosols were almost completely absent. The relatively unchanged appearance of the eye and appearance of discrete cloud features within the hexagon can also be seen in the June 2013 and April 2017 mosaics in Fig. 2.

Here we present a more extensive analysis of the north polar region, covering a wider range of latitudes from inside the eye to just outside the hexagon, allowing us to define the characteristics of the polar cloud bands and their temporal evolution during Saturn’s approach to its May 2017 northern summer solstice. Our analysis is based primarily on observations of the Cassini Visual and Infrared Mapping Spectrometer (VIMS) and to a lesser degree on the bandpass filter observations of the Cassini Imaging Science Subsystem (ISS). VIMS is unique in covering both visual and near-IR spectral bands and providing constraints from both reflected sunlight and thermal emission by Saturn. We first describe the observations we used, followed by a description of our vertical structure and composition model, and next a description of our radiation transfer model. We finally describe the results of fitting models to the spectral observations and their implications for the evolution of aerosols and color in Saturn’s north polar region, as well as changes in the vertical distribution of phosphine.

2. ISS OBSERVATIONS

2.1. ISS instrument characteristics and data reduction

The Cassini Imaging Science Subsystem (ISS) is described by Porco et al. (2004). It has a narrow angle camera (NAC) with a field of view (FOV) 0.35° across, and a wide angle camera (WAC) with a FOV of 3.5°, both using 1024-pixel square CCD arrays with pixel scales of 1.24 and 12.4 arcseconds/pixel respectively (in the unbinned imaging mode). For our analysis we used WAC images (identified in Table 1) to provide the best combination of spatial resolution and...
polar latitude coverage as well as samples of short and long wavelength continuum filters, as well as an intermediate methane band. The image files were retrieved from the NASA Planetary Data System’s Imaging Node and processed with the USGS ISIS 3 cisscal application, which is derived from the IDL cisscal application developed by the Cassini Imaging Central Laboratory for Operations (CICLOPS). This cisscal application produces images in I/F units (the ratio of target brightness relative to that of a unit-albedo Lambertian reflector illuminated and viewed normally at the same distance from sun). Ephemeris and pointing data allowing transformations between image and planet coordinates are disseminated by NASA’s Navigation and Ancillary Information Facility (Acton 1996).

The penetration depths of selected ISS filters we used are illustrated in Fig. 3, where normalized filter transmissions are overlaid on a plot of the pressure at which the 2-way vertical optical depth in a clear atmosphere reaches unity. The violet (440 nm) filtered image is unaffected by methane absorption, and in a clear atmosphere would record high I/F values produced by Rayleigh scattering over large optical depths. But in Saturn’s atmosphere a UV-absorbing haze decreases shortwave reflectivity and produces the tan color characterizing most of Saturn. The MT2 (727 nm) and MT3 (890 nm) filters sample intermediate and strong methane bands, and are mainly sensitive to scattering by upper tropospheric and stratospheric hazes respectively. The CB2 filter samples a continuum wavelength which is sensitive to aerosol scattering originating at the several bar level, is much less sensitive to Rayleigh scattering, and only weakly sensitive to absorption by methane and hydrogen collision-induced absorption (CIA). At the incident solar angles applicable to polar observations, these penetration depths reach pressures that are often a factor of two or more smaller. For the quantitative analysis we describe in later sections, the viewing and illumination geometry is fully accounted for. Here we make use of Fig. 3 for qualitative interpretations described below.

2.2. ISS characterization of Saturn’s north polar region.

The basic morphologies of Saturn’s north polar cloud features as it approached its northern summer solstice are displayed in Fig. A using ISS wide angle camera images taken on 13 June 2013 (panels A-C) and on 3 December 2016 (D-F). The main features in 2013 are the eye region (bright in A, and dark in B and C), which is about 1.2° in radius, an intermediate region interior to the hexagon (generally dark in B-C and E-F), but bright in (A and D), which extends out to about 75°N in planetocentric latitude, and a middle band (bright in B) that extends from the hexagon out to 63.5°N. A similar morphology is present in 2016 images, but there are significant differences with respect to wavelength, latitude, and time that provide important clues regarding the nature of the cloud structure within this region. These are interpreted with the help of penetration depth calculations displayed in Fig. 5.

2.2.1. Qualitative interpretation of 2013 ISS images.

In the violet image of Fig. A, the interior of the hexagon is much brighter than the surrounding clouds, which will later be shown to be a result of reduced aerosol absorption and greater visibility of Rayleigh scattering. A strikingly different appearance is provided by the 727-nm image in panel B, where the interior of the hexagon is seen to be darker than surrounding clouds. Here methane absorption provides a dark background that is not brightened much by the smaller amounts of high altitude aerosols available to scatter light above that absorption. The central eye region is especially dark due to even smaller amounts of aerosol scattering. Another strikingly different appearance is seen in the 752-nm image in panel C. Because methane absorption is relatively weak at this wavelength, deeper discrete bright cloud features can be seen through the relatively translucent overlying aerosol layers. Near-IR observations show that these discrete features are associated with enhanced scattering in the ammonia ice layer, as seen for similar features found in the south polar region (Stromovsky et al. 2020a). The significant depth of these features is evident from their nearly complete absence from the images with significant Rayleigh scattering (panel A) or significant methane absorption (panel B). Note that there seem to be two hexagonal boundaries in the 2013 images (most visible in panel B): one just poleward of the 75°N contour and a second just outside that contour. The inner boundary is the most sharply defined for all three wavelengths.

2.2.2. Qualitative interpretation of 2016 ISS images.

Panels D-F of Fig. B provide views of the same region at the same wavelengths but almost 3.5 years after the views in panels A-C. The violet image in panel D shows that a dramatic change has occurred in the upper aerosol layers during that interval. The bright region inside the hexagon has darkened dramatically due to the increased abundance of absorbing aerosols, with the exception of the small eye region, which has apparently not seen much of an increase in aerosol absorption. (Although the eye seems brighter in D than in A, this is due to a change in the image enhancement.) Nor has the eye seen an increase in aerosol scattering, which is evident from the fact that it remained dark in the 727-nm image in panel E. Another region that has seen an increased amount of upper level aerosols is the region between the hexagon boundary (around 75°N planetocentric) and the 63.5°N contour, which has gotten darker in violet (due to more aerosol absorption at short wavelengths) and brighter in the 727-nm image due to more aerosol scattering at longer wavelengths where chromophore absorption is not important.

In panel D of Fig. B, the polar region from 63.5°N to 75°N is relatively dark compared to its surroundings, with an increase in I/F at the edge of the hexagon near 75°N, and another increase at 63.5°N. Hazes in-
Fig. 2.— In the left panel, taken from NASA press release PIA21049, are color composite images of the north polar region from 2012 and 2016, during which the color inside the hexagon appeared to change from blue to orange. A remapped polar stereographic view of the transition, taken from NASA press release PIA21611, combined wide-angle camera images in red, green, and blue filters to produce these approximations of natural color views. The original images have a resolution of about 80 km/pixel (2013) and 80-14 km/pixel (2017), while the remapped images both have a scale of 25 km/pixel.

**TABLE 1**

| ISS image ID   | ISS Filter | UT Date   | YYYY-DAY | Time          | Pixel size (km) | Phase angle (°) | Fig. ref. |
|---------------|------------|-----------|----------|---------------|-----------------|----------------|----------|
| W1749823714   | VIO (440 nm) | 2013-164  | 13:13:05.936 | 68.6          | 94.7            | 4A               |
| W1749823766   | MT2 (727 nm) | 2013-164  | 13:13:57.563 | 68.6          | 94.7            | 4B               |
| W1749823807   | CB2 (752 nm) | 2013-164  | 13:14:39.035 | 68.6          | 94.7            | 4C               |
| W1859479945   | VIO (440 nm) | 2016-338  | 17:05:17.086 | 152.9         | 96.2            | 4D               |
| W1859479996   | MT2 (727 nm) | 2016-338  | 17:06:08.150 | 152.9         | 96.1            | 4E               |
| W1859480030   | CB2 (752 nm) | 2016-338  | 17:06:42.169 | 76.4          | 96.1            | 4F               |

1Observation IDs are ISS_192SA_NPOLMOV001_VIMS (2013) and ISS_251SA_NPOLMOV001_VIMS (2016).
filter (752 nm) being much less sensitive to scattering by small haze particles that dominate the appearance at shorter wavelengths.

2.2.3. Changes in the hexagon boundary

An odd result of the 2013-2016 comparison in Fig. 4 is that the hexagon seems to have increased in size between 2013 and late 2016, with its outer boundary seemingly moving from a position well inside the 75°N latitude circle in 2013 to essentially straddling it at the later date, most easily seen in comparing the CB2 filter images (Fig. 4C and F). The situation is more complicated for the other two filters, both of which seemed to have an extra band of darker brightness (panel D) or intermediate brightness (panel E) with an inner boundary inside the 75°N circle and an outer boundary outside the circle. It appears that by late 2016 both boundaries moved closer to the 75°N circle.

2.2.4. Color changes

The northern polar region’s transition from winter to summer included the formation of what Sayanagi et al. (2016) called a bright polar hood (see Fig. 2), which we will see is also connected to the previously noted color change inside the hexagon, from blue/green to a more golden color. A much smaller effect was seen in the small eye region, where the color remained blue/green over the entire period. Two factors that might contribute to the different behavior of the eye are (1) the region closest to the pole is the least exposed to sunlight and thus haze production would be lower and (2) as suggested by the sharp boundary of the eye region, there may be a dynamical effect similar to what is seen at the eye of an earthly hurricane, namely a downwelling that keeps the region relatively free of upper level aerosols. Such a downwelling has also been invoked, e.g. by Fletcher et al. (2008), to explain warm temperatures and depleted PH₃ gas. A more accurate description of the color changes is provided by VIMS spectral observations.

3. VIMS OBSERVATIONS

3.1. VIMS instrument characteristics and data reduction

The Visual and Infrared Mapping Spectrometer (VIMS) includes two separate spectrometers. As described by Brown et al. (2004), the so called visual spectrometer covers the 0.35-1.05 μm spectral range using 96 bands with a 7.3-nm spacing, and the near-IR spectrometer covers the range of 0.85-5.12 μm using 256 contiguous channels sampling the spectrum.
at intervals of approximately 0.016 μm. The instantaneous field of view of each pixel pair, as combined in the observations we used, covers 0.5 × 0.5 millidadians, and a typical frame has dimensions of 64 pixels by 64 pixels. Due to effects of order-sorting filter joints, we avoided comparisons between models and observations at the most strongly affected regions near 1.64 μm and 3.85 μm, but found that the effects of the 2.98-μm joint produced only a relatively small local depression of about 10%, which was not a significant issue (Stromsky et al. 2013).

The VIMS data sets we selected (identified in Table 3.2) provide an efficient combination of spatial coverage from the north pole out to just beyond the hexagon boundary, and at the same time sufficient spatial resolution to resolve key aerosol features. These data were reduced using the USGS ISIS3 (Anderson et al. 2004) vimsCal program, which was derived from the software provided by the VIMS team (and is available on PDS archive volumes). We used the RC19 calibration as described by Clark et al. (2018), with the exception that we had to correct serious errors in how the RC19 visual spectrometer calibration was implemented in the ISIS3 software. These corrections are described later in Sec. 3.4.2. Conversion to I/F (reflectivity relative to a normally illuminated Lambertian reflector) used the solar spectrum packaged with the ISIS3 and PDS-supplied software, which is now based on a more modern solar reference described by Thompson et al. (2015). Computation of planet coordinates and illumination parameters for each pixel of a VIMS cube utilized kernels supplied by JPL NAIF system and SPICELIB software (Acton 1996).

3.2. VIMS visual channel observations

VIMS visual channel observations of Saturn’s north polar region in June 2013 and November 2016 are shown in Figs. 3 and 4 respectively. These display spatial structure and spectral variations consistent with the ISS bandpass filter images displayed in Fig. 2 and Fig. 4. For both VIMS observations we used the full spectrum to compute tristimulus values (the RGB primary multipliers) using CIE1931 color matching functions (CIE1932) and the natural color using the IEC61966-2-1 standard sRGB color space with a D65 white reference (IEC1999). This provides greater accuracy than is possible with bandpass filters, although color differences between our results and the press release results in Fig. 2 are not very significant. Our VIMS-based color images are shown in panel G of both figures, using a linear stretch from zero, without attempting to correct for illumination changes across the images. These confirm that the region transformed from a blue/green color in 2013 to a gold color near the end of 2016, except for the eye, which remained relatively unchanged in color and somewhat more blue than the rest of the hexagon interior in 2013.

All the spectral samples show a significant drop in I/F at wavelengths below 570 nm, by a factor of two or more by 400 nm. That decline is due to particulate absorption, probably in a photochemical haze, and gives Saturn its overall tan color. What compound is responsible for that absorption is unknown. Possible candidates are discussed by West et al. (2009) and refer to the same possible candidates discussed for Jupiter’s red chromophore by West et al. (1986). We will later show that the red chromophore needed for Saturn is likely significantly different from that which works well on Jupiter.

The 2013 spectral samples taken inside the hexagon (but outside the eye) have a similar shape characterized by a strong downward gradient from green to red. This is qualitatively consistent with scattering by relatively small particles (a combination of Rayleigh scattering and small-particle haze scattering). Their declining peak I/F as the pole is approached is mainly due to declining illumination as the terminator is approached (near the lower right). In panel A, for which we used a Minnaert function to approximately correct for changes in viewing and illumination across the image, we see that the entire region inside the hexagon is of similar brightness at short wavelengths, as we saw in the ISS image centered at a similar wavelength in panel A of Fig. 4.

The spectral samples taken from the 2016 VIMS visual observations (Fig. 6) present a different picture in which the spectra inside the hexagon look more like the spectrum taken just outside the hexagon, except for the eye spectrum, which has a strong downward gradient from green to red that accounts for the blue/green color of the eye in panel G. Due to relatively constant illumination for the chosen spectral samples, those spectra interior to the hexagon are much more similar than the corresponding samples from 2013. This is qualitatively consistent with increased aerosol scattering by relatively larger particles, presumably generated by photochemistry, although the lack of any obvious latitudinal gradient contradicts the idea that haze production might be proportional to the local solar incident UV flux. It is consistent with haze production depending on the daily mean actinic flux, which is less dependent on the solar zenith angle.

The discrete bright features seen at continuum wavelengths are relatively deep given their low contrast at 725 nm and their disappearance at 894 nm. We will later show that they are indeed ammonia ice clouds seen underneath the translucent overlying haze. The main exception is the bright spot at the left edge of the 2013 images, which has a spectrum (not shown) that is similar to that of the clouds outside the hexagon, and extends high enough to be seen at 894 nm. This feature is not as apparent in color images, especially without a hard stretch. It can be seen in the 2013 mosaic of Fig. 2 about 80% of the distance from the pole to the hexagon boundary along a line 45° CCW from vertical. The feature does not appear to be present in 2016 images.

3.3. VIMS near-IR north polar observations

3.3.1. Near-IR overview
TABLE 2
OBSERVING CONDITIONS FOR VIMS VIS AND IR DATA CUBES WE USED TO CONSTRAIN MODELS.

| Observation ID | Cube Version | UT Date Start/End Pixel Phase Fig. Ref. |
|----------------|--------------|--------------------------------------|
| 192SA_NPOLVORT001 | V1749893170_1 | 2013-06-14 08:30:42.07 08:39:22.16348 km 46.06° | 57 |
| 249SA_NPOLMOV001 | V1858161491_1 | 2016-11-18 10:51:12.07 10:58:25.56 312 km 78.95° | 68 |

The full observation ID has a prefix VIMS and suffix PRIME for row 2. Cube IDs have suffixes _ir and _vis to distinguish near-IR and visual cubes.

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**Fig. 5.**—VIMS 14 June 2013 visual channel images (A-F), a natural color image (G) computed from the spectrum at each pixel, and selected visual spectra (H) from locations circled and numbered in images A-F. The spectral observations were destriped using smoothed 7-column averages to reduce column-to-column offset changes, as described by Adriani et al. (2007), except for \( \lambda < 0.46 \mu m \) for which we used a median instead of an average. The vertical dashed lines in H indicate wavelengths of images in panels A-F. Numbered circles mark locations from which modeled spectra were extracted.

The VIMS near-IR views of Saturn’s north polar region in late 2013 and in 2016 are displayed in Figs. 7 and 8, respectively, where we show images at six sample wavelengths and a color composite in which ammonia ice clouds attain a magenta color (the composite assigns R and B to continuum wavelengths and G to a wavelength at which ammonia ice is a strong absorber, so that where ammonia ice is present there is a lack of green, which creates magenta as the sum of red and blue). Panels A, C, and E show continuum wavelength 1.58 \( \mu m \) and pseudo continuum wavelengths 2.73 \( \mu m \) and 4.08 \( \mu m \), respectively. As evident from the penetration depth profile displayed in Fig. 9, these are at wavelengths of local minima in gas absorption,
allowing the deeper views of aerosol scattering contributions. A deep penetration is also available at 5.05 \( \mu \text{m} \) (shown in panel F), but Saturn’s thermal emission at this wavelength greatly exceeds scattered sunlight, and is controlled by the blocking effect of deep aerosol layers. The bright regions in panel F are where this blocking effect is greatly reduced by a lack of deep absorbing aerosols. Perhaps surprisingly, the eye is not a region of unusually high emission in either 2013 or 2016, or in 2008 (Baines et al. 2009b), indicating that, at least at these times, it is not clear of aerosols down to the 5 bar level. Thus, if descending motion is responsible for the relative clarity of the upper troposphere within the eye, that descent does not continue much below the several bar level.

3.3.2. 5-\( \mu \text{m} \) emission features

There are also strong patterns in the 5-\( \mu \text{m} \) emission that are either very muted or undetectable in the upper tropospheric clouds seen in panels A, C, and E of Figs. 7 and 8. Perhaps the most prominent of these is the dramatic bright ring of emission seen in 2016 (Fig. 8F), which intersects numbered circle 5 (near 86°N). This region is only slightly darker in panels A and C, and unremarkable in panel E. A similar example can be found by comparing locations 7 and 8. These locations appear equally bright in images A-E, but show a large difference in 5-\( \mu \text{m} \) emission levels in panel F. On the other hand, there are cases where there is a strong correlation between features at these different wavelengths. A prominent example is between the dark ring of low emission in F (near 87°N, intersecting location 4) and the bright ring of clouds in panels A, C, and E, which appear as magenta (ammonia ice-signature) clouds in G, both of which are indicators of increased cloud optical depth. However, the brightness modulations at 5 \( \mu \text{m} \) appear to be occurring in a deeper layer than those in the upper troposphere, as also inferred from a quantitative analysis of Saturn’s south polar cloud structure (Sromovsky et al. 2020a).
3.3.3. Near-IR changes between 2013 and 2016

The near-IR views of the north polar region provide a much different and more dramatic picture of the aerosol changes that occurred between 2013 and 2016 (Figs. [7] and [8]). At near-IR wavelengths the inside of the hexagon was much darker in 2013 than in 2016. The lack of aerosol scattering in 2013 is much more dramatic in the near-IR than in the visible because in the latter case the lack of aerosol contributions is seen against a bright background of largely conservative Rayleigh scattering, while in the near-IR the background is much darker due to gaseous absorption, primarily by methane. In 2013 the near-IR spectrum of the eye showed a falloff with increasing wavelength that is similar to that seen in 2016, but even a bit steeper. The greatest spectral difference between these two times is in spectra from the interior of the hexagon. In 2013 the mid-hexagon spectra are much more similar to the eye spectrum than to the spectrum outside the hexagon. They also show a steep falloff of I/F with increasing wavelength, though not quite as steep as for the eye spectrum.

Different results are seen in 2016 (Fig. [8]). In this case spectral samples between the eye and the outer hexagon boundary (e.g. 5 and 7) are very similar to each other (ignoring the thermal emission difference beyond 4.6 μm), and in spectral shape very similar to the spectral sample (10) from just outside the hexagon. They are just slightly lower in I/F, partly a result of reduced illumination. Their lack of a strong decline in continuum I/F with wavelength is indicative of relatively large aerosol particles compared to what is normally seen in stratospheric hazes. The spectrum from the eye is dramatically different: continuum I/F values decline rapidly with wavelength, disappearing into the noise at 4.08 μm. What little aerosol scattering is produced inside most of the eye appears to arise from small particles, and there the optical depth of aerosol contributions must be very low. However, analysis of close-up observations of the eye by Baines et al. [2018] have found exceptionally large particles in a bright discrete ammonia-signature feature in this region.

There are some other noteworthy differences in the morphology and discrete features between 2013 and 2016. The 14 June 2013 observations captured an unusual discrete feature that is bright in the 1.993-2016. The 14 June 2013 observations captured an un

3.4. Combining visual and near-IR spectral observations

We initially tried to constrain the vertical cloud structure of the polar regions from just the near-IR VIMS observations, but there are significant advantages in carrying out a combined fit to both spectral ranges simultaneously. While the near-IR region offers the advantages of a variety of methane band strengths, accurate line-by-line correlated-k models covering much of the range, sensitivity to greater depths and to thermal emission in the 5-μm region, sensitivity to trace gases, and a wavelength range insensitive to Rayleigh scattering in favor of aerosol scattering, there are also significant advantages to the visual spectral range. These include much greater sensitivity to very small particles, sensitivity to the chromophore that provides most of Saturn’s color, and to its vertical location, as well as sensitivity to Rayleigh scattering at wavelengths where methane absorption is negligible. However, there are two problems in combining visual and near-IR spectral observations: differences in spatial sampling and potential differences in calibration.

3.4.1. Accounting for spatial sampling differences

The first problem with combined analysis is that the two spectrometers have slightly different fields of view and are not precisely bore-sighted. According to Brown et al. [2004] the near-IR FOV is 0.495±0.003 mrad, while the visual FOV is 0.506±0.003 mrad. The bore-sight misalignment pre-launch was less than 0.3 pixels, but in 1999 (in flight) the IR-VIS offset was found to be -1 pixels in the X direction and +2 pixels in Y. And in 2001 it was measured to be -1 and 0 respectively (Brown et al. [2004]). Using the spectral region where the VIMS-VIS and VIMS-IR bands overlap, we estimate, for the 2013 and 2016 cubes we analyzed, that the VIS - IR offset is closer to 2 pixels in X and 1.5 in Y.

Fig. [10] illustrates the effects of different image scales and bore-sighting offsets. However, it also shows that when sampled at the same planet locations, the I/F differences are small. They are also small in regions of spatial homogeneity. Thus our approach to spatial sampling is to take pixels that are closest to the same position on the planet and avoid regions of large pixel-to-pixel variations. The pixel closest to the north pole in 2013 visual images of Fig. [5] is at x = 29 and y = 13, which is centered at 89.62°N and 322.43°E, while in the near-IR images of Fig. [7] the pixel closest to the pole is at x = 28 and y = 11, centered at 89.72°N and 318.39°E. Near the pole, a displacement of 1 pixel away from the pole corresponds to a difference in latitude of 0.37°. This makes it difficult to obtain accu
rate combined spectra for small discrete features, but less of a problem for regions that are locally homogeneous or slowly varying from pixel to pixel, which are the regions we try to sample.

3.4.2. Accounting for calibration differences

Potential differences in radiometric calibrations were investigated by comparing visual and near-IR spectra in the spectral overlap region between 0.88 µm and 1.05 µm. However, it is first necessary to correct the latest RC19 visual channel calibration because the ISIS3 VIMSCAL implementation failed to include a multiplier that is essentially the inverse responsivity of the visual detector array. The multiplier that was included for both visual and near-IR instruments is displayed in Fig. 7 of the final VIMS calibration report (Clark et al. 2018). The IR portion includes the inverse responsivity factor, but the visual portion (the first 96 values) did not. Instead, it includes the ratio of RC19 to RC17 inverse throughputs (RC17 and RC19 refer to earlier and later radiometric calibrations of the VIMS instrument), which appears to be mainly just the ratio of the new solar reference (Thompson et al. 2015) to the prior solar reference (Thekaekara 1974) that was used in the RC17 calibration. Fortunately, the correct multiplier accounting for detector responsivity was available. Inserting that multiplier into the ISIS3 calibration code yields visual I/F spectra that are very similar to those obtained from the RC17 calibration, except somewhat smoother and smaller by a factor of about 0.95 over most of the spectral band. The radiance (termed specific energy) cubes were changed more significantly than the I/F cubes, roughly in accord with the difference between the old and new solar references. The new solar reference was also used in the near-IR VIMS spectrometer calibration. Although
there is a substantial difference in the near-IR between the two solar references, this did not lead to a large change in I/F spectra because of other changes in the calibration. However, it did lead to 10-20% decreases in the radiances near 1 µm and near 3 µm respectively. With the RC19 visual channel calibration corrected,
we can then make meaningful comparisons of visual and near-IR I/F spectra in the overlap region from 980 nm to 1050 nm. Two comparisons are shown in Fig. 11 in the left panel for a 2013 average (over the lower box in the upper right panel of Fig. 10) and in the right panel for a 2016 average (over the upper box in the lower right panel of Fig. 10). Because of response falloff at the edges of their respective spectral ranges, the near IR results (red, +) are least reliable at the shortest wavelength and the visual results (open circles) are least reliable at the longest wavelengths. Some of the difference between the two spectra are due to lower resolution of the near-IR spectrometer. Also note that the near-IR wavelengths have shifted relative to the visual channels between 2013 and 2016. The agreement between the 2016 spectra is remarkably good, and provides little evidence for a discrepancy. The 2013 comparison is less comforting but does not provide sufficient justification for changing either of the calibrations. To create a single spec-
trum that joins the visual and near-IR into a single spectrum, we chose to join the spectra in the middle of the overlap region, using the visual spectrum for wavelengths less than 970 nm and the IR spectrum for wavelengths longer than 970 nm. After completion of model fits, we found that a joint at 940 nm instead of 970 nm would have improved fit quality somewhat.

3.4.3. Noise and offset estimates

Sromovsky and Fry (2010b) investigated near-IR VIMS noise levels by comparing observations of Jupiter taken just 2 minutes apart, and found standard deviations of measurements of the same location on Jupiter were only of the order of 0.1-0.2% for moderate to high signal levels. That noise level is well below other sources of uncertainty. Their crude I/F noise estimate for very low signal levels was $\sim 5 \times 10^{-4}$, which is worth accounting for. We tried to make new noise level estimates in two ways, first by measuring the standard deviation of adjacent measurements in relatively spatially smooth regions. Because spatial smoothness is also a function of wavelength, this was not effective at all wavelengths. The most reliable results were obtained at wavelengths for which the measured I/F was not significantly larger than the noise level. Better results were obtained from cubes containing a view of space. The standard deviation of nine space measurements (also in I/F units) roughly containing a view of space. The standard deviation of noise level. Better results were obtained from cubes the measured I/F was not significantly larger than the noise level. Their crude I/F noise estimate for very low signal levels was $\sim 5 \times 10^{-4}$, which is worth accounting for. We tried to make new noise level estimates in two ways, first by measuring the standard deviation of adjacent measurements in relatively spatially smooth regions. Because spatial smoothness is also a function of wavelength, this was not effective at all wavelengths. The most reliable results were obtained at wavelengths for which the measured I/F was not significantly larger than the noise level. Better results were obtained from cubes containing a view of space. The standard deviation of nine space measurements (also in I/F units) roughly followed an analytical model for which $SD_{\text{space}} = \exp(a + c \times (\lambda - \lambda_0)^3)$, with $a = -7.6$, and $c = 0.03$, for $\lambda_0 = 0.35 \, \mu\text{m}$. This model is displayed in comparison with the space observations in Fig. 12. This is also shown as the dashed component in Fig. 13. Although there are large discrepancies at wavelengths less than 1.3 $\mu\text{m}$, these are not significant compared to the signal levels in this part of the spectrum.

The I/F offset displayed in the top panel of Fig. 12 is apparently not valid for views of the planetary disk, suggesting that scattered light within the instrument might be a factor. Subtracting this offset from the spectra did not result in improved fit quality, and it is apparent from other considerations that there are offsets present in VIMS planetary spectra. Sromovsky and Fry (2010b) compared VIMS near-IR spectra of Jupiter to ground-based observations and HST NICMOS observations that indicated offsets of the order of 0.001 in I/F units at wavelengths near 2.4 $\mu\text{m}$. We also found indications of similar offsets, indicated by comparing deep minima in model spectra at 2.58 $\mu\text{m}$ with VIMS measurements of much reduced absorption depths that could not be matched by any model we tried that was consistent with other parts of the spectrum. Subtracting an offset of near 0.001 in I/F from the measured VIMS spectra substantially eliminated this discrepancy, as well as improved fits in other low I/F regions of the spectrum. However, the exact level of this offset is uncertain, and that uncertainty grows at shorter wavelengths, especially at visual channel wavelengths, where striping effects, even though largely corrected, do leave a residual uncertainty. The region between 0.85 and 2.5 $\mu\text{m}$ is a region that produces significant fitting errors that contribute a large fraction to $\chi^2$ when wavelength independent error models are assumed, and much of that is in the region of I/F minima, where offset uncertainties might be a significant factor. It is also possible that stray light and errors in modeling methane absorption are factors. To include all these effects in a way that balances the $\chi^2$ contributions more equally in wavelength, we used a wavelength dependent offset uncertainty model with a maximum of SDmax for $\lambda < 0.8 \, \mu\text{m}$ that is 6% of the mean I/F of the two spectral peaks between 1.2 and 1.4 $\mu\text{m}$. For $\lambda > 0.8 \, \mu\text{m}$, it declines as $(\lambda/0.8 \, \mu\text{m})^{-2.4}$ up to $\lambda = 2.4 \, \mu\text{m}$, beyond which it remains constant at that value. This second component (offset uncertainty) is shown by a thin solid line in Fig. 13. To these two components we added a fractional uncertainty of 0.08 times the observed spectral I/F. This third component is a crude estimate of the combined effects of calibration and modeling errors. These multiple uncertainty contributions are illustrated in Fig. 13.

3.5. VIMS combined visual and IR spectra

Our combined visual and near-IR spectra are illustrated in Figs. 14 and 15 for 2013 and 2016 observations respectively. In each figure twelve composite spectra are plotted for image locations illustrated in three images: a visual composite, a near-IR composite, and a thermal emission at 5.2 $\mu\text{m}$ monochromatic image. The first 10 of these spectra are from the same locations identified in previous figures. For the 2013 observations, the spectra within the hexagon are seen to be relatively dark, with the main exceptions being for a discrete ammonia cloud (spectrum 11). For the 2016 observations, the spectra within the hexagon are generally significantly brighter, except for the inner...
eye region, which is the only truly dark region.

4. RADIATIVE TRANSFER MODELING

Our parameterization of atmospheric composition and the vertical distribution and scattering properties of aerosols, our modeling of gas absorption, and our treatment of multiple scattering and thermal emission generally follow Sromovsky et al. (2020a), the main exception being that we here analyze combined visual and near-IR spectra. Our model parameters for this study are listed and described in Table 3. Model parameters were constrained in a two-step process. First, we used trial and error calculations guided by sensitivity studies to form a crude initial fit. These initial guesses were dramatically refined using a form of the Levenberg-Marquardt non-linear regression algorithm described by Press et al. (1992), which also provides uncertainty estimates for the model parameters based on spectral measurement uncertainties. In fitting model spectra to observed VIMS spectra we omitted the 1.61–1.68 µm region to avoid the effects of an order-sorting filter joint, and also the 2.2–2.4 µm and 3.18–3.95 µm regions due to their very poor signal to noise ratios. In the following subsections we describe our assumed atmospheric structure and composition, gas absorption models, parameterization of cloud structure, parameterization of chromophore absorption, constraining deep cloud composition, constraining of chromophore location, and estimation of sensitivity to model parameters and to initial guesses.

4.1. Atmospheric structure and composition

We used Lindal et al. (1985) to define the temperature structure between 0.2 mbar and 1.3 bars, and approximated the structure at deeper levels using a dry adiabatic extrapolation. We also assumed their value of 0.0638 for the He/H₂ number density ratio, which is within the 0.04-0.075 range recently derived from Cassini Composite Infrared Spectrometer observations by Achterberg and Flasar (2020). Our assumed nominal composition of the atmosphere as a function of pressure is displayed in Fig. 16. For methane we chose the Fletcher et al. (2009b) VMR value of (4.7 ± 0.2) × 10⁻³, which corresponds to a CH₄/H₂ ratio of 5.3 × 10⁻³. For CH₃D we also used the Fletcher et al. (2009b) VMR value of 3 × 10⁻⁷. We assumed an ammonia vapor profile with a deep uniformly mixed region for P > 4 bars with a VMR of 400 PPM, another uniformly mixed region with a lower VMR between 4 bars and the ammonia condensation pressure, above which we assumed that the ammonia VMR followed a saturated vapor pressure profile up to the tropopause, and above that we again assumed a uniform mixing ratio. This profile is illustrated by the dot-dash line in Fig. 16. It was inspired by the results of Briggs and Sackett (1989) who found a deep mixing ratio of 480 ± 100 ppm and a depleted mixing ratio of 70-110 ppm near 2 bars. We chose a somewhat lower deep value that is roughly in the middle of the Laraia et al. (2013) limits of 360-480 ppm. However, the only NH₃ profile parameter that our VIMS observations are sensitive to is the mixing ratio in the depleted region, which is presumably produced by the formation of an NH₃SH cloud near 4 bars. Our initial attempts to fit that parameter resulted in very low values with very high uncertainties. We thus assumed in our first round of latitude dependent fits a fixed value of 12 ppm, which we chose to produce an ammonia condensation pressure near 1 bar because that is close to the upper limit of the base pressures we found for the ammonia cloud layer.
We subsequently learned that it was mainly the 2016 observations that presented fitting problems. It appears that the VIMS sensitivity to the ammonia mixing ratio decreases substantially wherever upper level aerosol opacity is high, leading to at least poor uncertainty estimates, and perhaps also erroneously low VMR values. For the 2013 observations, for which the upper tropospheric aerosol opacity is low, we were able to obtain reasonably well constrained fits, and we thus included our NH\textsubscript{3} fits in our final results.

Other spectroscopically important gases that were constrained by our fits to VIMS observations included arsine (AsH\textsubscript{3}) and phosphine (PH\textsubscript{3}). We fit an adjustable vertically uniform mixing ratio for Arsine and, following Fletcher et al. (2009a), we parameterized the PH\textsubscript{3} VMR profile using three parameters: a deep mixing ratio \(\alpha_0\), a break point pressure \(p_b\), and a ratio \(f\) of the PH\textsubscript{3} scale height to the pressure scale height. At pressures less than \(p_b\), the PH\textsubscript{3} mixing ratio can be written as

\[
\alpha(p) = \alpha_0(p/p_b)^{(1-f)/f} \quad \text{for} \quad p < p_b.
\]

Because we found a high correlation between spectral effects of \(p_b\) and \(f\), only two of our three parameters could be well constrained by the VIMS observations.
Because our attempts to fit all three parameters usually resulted in low (but poorly constrained) values of $f$, we chose to fix $f$ at 0.1, and decided fit the other two parameters. Our fixed value of $f$ is at the low end of the range of values found by Fletcher et al. (2011) when they assumed a fixed breakpoint pressure.

4.2. Gas absorption models

We used gas absorption models described by Sromovsky et al. (2018) and Sromovsky et al. (2013) and references cited therein. For methane we used correlated-k models based on line-by-line calculations down to 1.268 $\mu$m (Sromovsky et al. 2012), but for shorter wavelengths used correlated-k fits to band models of Karkoschka and Tomasko (2010) (we used P. Irwin’s fits available at [http://users.ox.ac.uk/~atmp0035/ktables/](http://users.ox.ac.uk/~atmp0035/ktables/) in files ch4_karkoschka_IR.par.gz and ch4_karkoschka_vis.par.gz). The NH$_3$ absorption model fits are from Sromovsky and Fry (2010a), which are based primarily on band models of Bowles et al. (2008). Absorption models for phosphine (PH$_3$) and arsine (AsH$_3$) are the same as described by Sromovsky et al. (2013). Collision-induced absorption (CIA) for H$_2$ and H$_2$-He was calculated using programs downloaded from the Atmospheres Node of the Planetary Data System, which are documented by Borysow (1991, 1993) for the H$_2$-H$_2$ fundamental band, Zheng and Borysow (1995) for the first H$_2$-H$_2$ overtone band, and by Borysow (1992) for H$_2$-He bands.
TABLE 3
CLOUD AND GAS MODEL PARAMETERS USED IN SPECTRAL CALCULATIONS.

| Param. (unit) | Description | Value |
|--------------|-------------|-------|
| $p_1$ (bar)  | stratospheric haze base pressure | adjustable |
| $r_1$ (µm)  | effective radius of stratospheric particles | adjustable |
| $n_1(λ)$    | refractive index of stratospheric particles | $n_1 = 1.4 + i \times n_1(λ)$ |
| $r_3$ (µm)  | effective radius of main cloud particles | adjustable |
| $n_3(λ)$    | refractive index of main cloud | adjustable |
| $r_4$ (µm)  | effective radius of deep cloud particles | adjustable |
| $n_4(λ)$    | refractive index of deep cloud particles | $1.6 + i \times n_4(λ)$ |
| $p_2$ (bar)  | base pressure of putative NH$_3$ cloud | adjustable |
| $n_2(λ)$    | refractive index of NH$_3$ cloud particles | adjustable |
| $r_3$ (µm)  | optical depth of upper cloud at 1 µm | adjustable |
| $n_3(λ)$    | optical depth of NH$_3$ cloud at 1 µm | adjustable |
| $p_4$ (bar)  | base pressure of deep cloud (NH$_2$SH + H$_2$O ?) | adjustable |
| $n_4(λ)$    | refractive index of deep cloud particles | adjustable |
| $r_4$ (µm)  | optical depth of deep cloud at 1 µm | adjustable |

| Parameter | Value |
|-----------|-------|
| NH$_3$V1 | NH$_3$ VMR for Pcond < P < 4 bars | 12 ppm or adjustable |
| $p_b$ (bar) | PH$_3$ break-point pressure | adjustable |
| $n_0$ | PH$_3$ volume mixing ratio for $p > p_b$ | adjustable |
| $f$ | PH$_3$ to H$_2$ scale height ratio for $p < p_b$ | fixed at 0.1 |
| AsH$_3$V | AsH$_3$ volume mixing ratio | adjustable |

NOTE: These compact cloud layers are assumed to have a top pressure that is 0.9 times the bottom pressure and a particle to gas scale height ratio of 1.0; aerosol particles are assumed to scatter like spheres with a gamma size distribution with variance parameter $b = 0.05$ for layers 1-3 and 0.1 for layer 4, with distribution function $n(r) = \text{constant} \times r^{i-3b}/(1-3b) \times \exp(-r/b)$, where $a = r_1$, for $i = 1, \ldots, 4$, and $b = \text{dimensionless variance}$, following Hansen and Travis (1974). Optical depths are given for a wavelength of 1 µm. $n_1(λ)$ and $n_2(λ)$ are either set equal to zero or adjusted using 2-3 free parameters in a model based on Eq. 2. The imaginary index $n_4(λ)$ is an empirical function discussed in Sec. 4.3. We also tried refractive indexes of NH$_3$SH and H$_2$O for layer 4.

Our parameterization of cloud structure diverges from the vertically diffuse layer structures of the type commonly used in prior publications. Instead, we here use a structure with four compact layers with fitted vertical positions and distinct compositions. In limited trials we found that somewhat thicker layers could improve fits to some spectra (an example is given in a later section), but others were best fit with compact layers. Compact layers also provided the best fits for Fletcher et al. (2011a) in modeling night-side 5-µm spectra, which were, however, insensitive to the stratospheric haze. But even in the polar stratosphere, there is some evidence for compact layers from limb observations (Sánchez-Lavega et al. 2020). While we think more effort in constraining layer thicknesses with VIMS spectra is likely to be productive, especially with improved signal/noise ratios from spatial averaging and/or center-to-limb analysis, this is a fairly complex topic that is left for future work. Using compact structures in this study avoids having to constrain both an upper boundary as well as a scale height for each layer, yet still allowed us to make accurate fits to the observations and leads to more stable solutions. Because we have many methane bands of varying strengths, we avoid ambiguities between pressure and optical depth, and also have such great sensitivity to vertical structure that our retrievals do not suffer much from the lack of center-to-limb constraints.

Our chosen layer compositions are partly based

![Fig. 16.](image) Volume mixing ratios (VMR) of spectroscopically important gases in the atmosphere of Saturn. These values were either assumed or derived from fitting the spectrum from the background cloud at location 2. The VMR for germane, to which VIMS is not sensitive, is from Bjoraker et al. (1986). See text for other VMR references. The dotted curve traces the saturation vapor pressure profile of NH$_3$. Horizontal gray bars show typical vertical locations of our four compact aerosol layers of distinctly different compositions.

4.3. Parameterization of cloud structure
on expectations from equilibrium cloud condensation (ECCM) modeling [Weidenschilling and Lewis 1973; Atreya and Wong 2005], as illustrated in Fig. 12. The lower aerosol optical depth in the polar regions and the wide spectral range of the VIMS visual and near-IR observations provide a unique capability to probe deeper layers as well as constrain composition to some degree. However, because the ECCM model does not provide a well defined composition for the stratospheric haze (which we generally found at an effective pressure of about 50 mbar) or the main upper cloud layer on Saturn (which we found to have an effective pressure at the 200-300 mbar level in the polar region), we needed to make some assumptions.

At least one of the top two layers is likely composed of a complex hydrocarbon that provides the short wavelength absorption responsible for Saturn’s generally tan color, which we will refer to as Saturn’s chromophore. We considered chromophores in either layer and both layers, but concluded from an analysis presented in Sec. 4.6 that the stratospheric haze alone was a viable location for the chromophore and provided the most convenient modeling behavior. We decided to model the stratospheric layer as a haze of spherical particles with an adjustable pressure, an adjustable optical depth, an adjustable radius, and a real and imaginary index parameterized to function as the chromophore, as described in Section 4.4.

The second layer, which is optically much thicker than the stratospheric haze, and is the main visible cloud layer in most regions on Saturn, appears to have no discernible ammonia ice spectral signature [Kerola et al. 1997] or any other near-IR spectral absorption features that could be used to identify it [Sromovsky et al. 2013]. A possible composition suggested by Fouchet et al. [2009] on photochemical grounds is diphosphine (P2H4), the optical properties of which are not known well enough to test this possibility. We also treated this layer as comprised of spherical particles with a real refractive index of 1.74, which is the value for P2H4 at 195 K according to Wohlfarth [2008]. We also found from test fits at a variety of locations that it generally produced slightly better fits than a real index of 1.4. Although we considered using an imaginary index with strong short-wavelength absorption (serving as the chromophore), our final fits treated this layer as non-absorbing over the VIMS spectral range.

The best justified composition is for the third layer, which is composed of NH3 ice, a conclusion based on detection of ammonia ice absorption features at 3-3.1 μm and near 2 μm and the fact that the fitted pressure of this layer are at a level where ammonia condensation is plausible for the fitted ammonia mixing ratio. An ammonia ice layer also fits well in models of south polar VIMS spectra [Sromovsky et al. 2020a]. The ammonia spectral signature can be readily seen in the north polar 2013 spectrum from location 2 (Fig. 13D) and much more dramatically in the spectrum from location 11 (Fig. 13E). Both of these provide further confirmation of our identification of NH3 ice as the composition of layer-3 particles, as discussed later in Section 6.3. We also modeled the scattering of this layer using a distribution of spherical particles with an adjustable effective radius and optical depth.

Because VIMS observations do not penetrate much deeper than the 5-bar level, our ability to constrain aerosols at the water cloud level is poor. Based on the work described in Sec. 4.5 which did not find acceptable fits using water ice or NH3SH, we selected a real index of 1.6, which is a somewhat arbitrary value between that of water ice and NH3SH, and a wavelength dependent imaginary index that crudely varied as some mix of these candidates, but provided generally more absorption, and seemed to provide a decent overall fit to the observations. Instead of following Sromovsky et al. [2020a] in assuming a fixed particle size, optical depth, and base pressure, with only an adjustable top pressure for the bottom layer, we here assumed spherical particles with an adjustable radius. We assumed that all layers were vertically thin. To avoid having to constrain four additional parameters, we used an adjustable base pressure and a top pressure 90% of the base pressure, which allows for layer overlap if necessary (conversion of our results to the case of more extended layers is discussed in Sec. 6.5).

For all layers we assumed a gamma size distribution [Hansen and Travis 1974] with a fractional variance b = 0.1 for the deep cloud of large particles and 0.05 for the other layers.

Later analysis reveals that the spectral effects of these layers are roughly as follows. Layer 1 controls the short-wavelength absorption and the depth of methane absorption bands. Layer 2 mainly controls the pseudo-continuum I/F values at wavelengths from about 700 nm to near-IR wavelengths. Layer 3 affects the I/F in the 2-μm and 2.7-3.1 μm region. Layer 4 has its main influence in limiting the I/F in the 4.7–5.1 μm emission region.

4.4. Parameterization of the chromophore absorption

Saturn requires some population of particles in the upper troposphere that absorbs strongly at short wavelengths in order to produce its generally tan color. It seems plausible that these chromophores consist of complex hydrocarbons created by the photochemical reactions driven by solar UV radiation. Candidate chromophores produced in laboratory experiments, such as the so called tholin material produced by Khare et al. [1993], the phosphorus compound produced by Noy et al. [1981], or the potential Jovian chromophore produced by Carlson et al. [2016], have all yielded materials with a strong UV absorption declining roughly log-linearly with wavelength to much lower baseline values at long wavelengths. This is also roughly the characteristic of the imaginary index for a Jovian chromophore inferred by Braude et al. [2018] from an analysis of center-to-limb spectra obtained by VLT/MUSE observations of Jupiter. These are compared with our model parameterizations in Fig. 18.
which are based on the functional form

\[
n_i(\lambda) = \begin{cases} 
n_i(0) + (n_{i,1} - n_{i,0}) \times 10^{-K_1(\lambda - \lambda_1)} & \lambda > \lambda_1 \\
n_{i,1} \times 10^{-K_2(\lambda_1 - \lambda)} & \lambda \leq \lambda_1 \\
0 & \lambda \leq \lambda_c
\end{cases} \quad \text{(2)}
\]

\[
n_i(\lambda) = \frac{1}{\Delta} \int_{\lambda - \Delta/2}^{\lambda + \Delta/2} n_i(\lambda') d\lambda' \quad \text{(3)}
\]

which defines a peak at wavelength \(\lambda_1\) and falloff rates away from the peak defined by log slope \(K_1\) on the long-wavelength side and \(K_2\) on the shortwave side. The zero value below wavelength \(\lambda_c = 0.15 \mu m\) ensures that the integral in Eq. (3) will remain finite. The box-car average defined by Eq. (2) produces a more rounded peak that better fits the I/F spectra for \(\Delta \approx 0.11 \mu m\). The chromophore characteristics so defined are compared with other chromophore models in Fig. 19. As evident in the figure, this parameterization can provide a decent fit to the suggested chromophore materials with appropriate choices of the model parameters. Since we know so little about the spectral character of the Saturnian chromophore it will be constrained by fitting the VIMS observations. The key parameters we adjust to fit model spectra are \(n_{i,1}, \lambda_1\) and the log slope \(K_1\). The other parameters \(K_2\) (which controls the rate of decline on the shortwave side of the peak) and \(n_{i,0}\) (which is the baseline absorption at long wavelengths) are not well constrained by the observations and usually set to somewhat arbitrary values of 20 \(\mu m^{-1}\) and \(5 \times 10^{-4}\) respectively. The latter value is in approximate agreement with the long-wavelength value inferred from modeling HST observations of Saturn by Sánchez-Lavega et al. (2020).

It also agrees with the minimum value inferred by Karkoschka and Tomasko (2005) for wavelengths below 700 nm, although it exceeds their estimated upper limit of \(10^{-4}\) for wavelengths near 1 \(\mu m\).

Because the imaginary index can reach significant peak values, we use a real index consistent with the Kramers-Kronig relation:

\[
n_r(\lambda) = n_{r,0} + \frac{2}{\pi} P \int_{0}^{\infty} \frac{\nu' n_i(\nu')}{\nu'^2 - \nu^2} d\nu' \quad \text{(4)}
\]

where \(\nu = 1/\lambda\) and \(P\) indicates the principal value of the integral that follows it, which we computed using Maclaurin’s formula (Oba and Ishida 1988). For \(n_{r,0}\), the real index at infinite wavelength (zero wavenumber), we ultimately adopted a value of 1.4, comparable to values expected for stratospheric hydrocarbons. Although none of the measured imaginary index spectra plotted in Fig. 18 captured a short-wavelength peak, a peak was observed near 400 nm in recent modeling of HST observations of Saturn (Sánchez-Lavega et al. 2020).

4.5. Constraining the composition of the deep cloud layer

The combination of visual and near-IR spectra provides an opportunity to better constrain the composition of the deep cloud that from an ECCM perspective might be dominated by \(\text{NH}_3\text{SH}\) or \(\text{H}_2\text{O}\) ice or a mixture of the two, as the deep layer has a significant effect on both short wavelength continuum I/F values as well as the region of thermal emission. Because these different compositions have different spectral absorption signatures (Fig. 19), we hoped to find which pro-
provided the best spectral fits. Using 2013 spectra inside the hexagon, which provided a better view of deeper layers because of reduced optical depth of the other layers, we found that water ice particles provided the worst fit and NH\textsubscript{4}SH particles a better fit, although neither provided as good a fit as the simple wavelength-independent refractive index model in which the index of the deep layer is given by \( n_d = 2 + 0.01i \). To minimize residual errors in the 0.8 – 1.7 \( \mu \text{m} \) region, we further improved that model by setting the real index to 1.6 (between that of H\textsubscript{2}O and NH\textsubscript{4}SH), and varying the imaginary index with wavelength as shown in Fig. 19. We adopted the imaginary index model labeled \( \alpha(\lambda) \) for the deep layer in carrying out the latitude dependent fits for both 2013 and 2016.

To investigate this further we considered four different composition models for the bottom cloud layer, all of which are plotted in Fig. 19: (1) our default synthetic model characterized by \( n_1 = 1.6 + i \times \alpha(\lambda) \), (2) a variant synthetic model for which \( n_4 = 1.6 + i \times b(\lambda) \), (3) NH\textsubscript{4}SH, and (4) H\textsubscript{2}O. We tried to constrain these models by fitting observed spectra from regions with low upper aerosol opacity so that the properties of the deep layer would be less attenuated. We chose a mid hexagon spectrum from 2013 location 5 (shown in Figs. 5, 7 and 14), which has a relatively high 5-\( \mu \text{m} \) emission (and presumably low deep cloud opacity) and another spectrum from location 2 in 2016, which has about half the 5-\( \mu \text{m} \) emission of the first case. The observed and fitted spectra are displayed in Fig. 20 for 3 of the four models. The best-fit parameter values for all of the models are listed in Table 4. The table shows that models (1) and (2) have closely similar parameter values and fit qualities, which is why model (2) was omitted from the spectral plots of Fig. 20.

The first column of Fig. 20 displays fits to the spectrum from 2013 location 5, which is in the middle of the hexagon, in a region with higher thermal emission and thus likely reduced deep cloud opacity. In this case NH\textsubscript{4}SH (\( \chi^2 = 318.40 \)) provides a better fit than water ice (\( \chi^2 = 370.88 \)), with our default synthetic index providing significantly better overall fit (\( \chi^2 = 279.48 \)), as well as beating them both in short wavelength and long wavelength subregions. We also fit these models to a 2016 spectrum from the middle of the hexagon (location 6) in a region with higher upper level aerosol opacity. In this case (not shown if Fig. 20) the three models all achieved comparable fit qualities, with our synthetic index providing the best fit, but only slightly better than NH\textsubscript{4}SH, which was only slightly better than H\textsubscript{2}O.

The second column of Fig. 20 displays results for location 2 in the eye region in 2016, which has a low burden of aerosols above the deep layer, but provides a significant attenuation of Saturn’s thermal emission, presumably due to the deep cloud. In this case models assuming a deep cloud made of H\textsubscript{2}O provided a somewhat better fit (\( \chi^2 = 379.49 \)) than a cloud made of NH\textsubscript{4}SH (\( \chi^2 = 491.99 \)), and both of these compositions were soundly beaten by our standard model (1) with \( \chi^2 = 282.11 \). Here the main advantage of H\textsubscript{2}O ice over NH\textsubscript{4}SH is in the thermal emission region, with \( \chi^2 \) contributions for \( \lambda > 4.5 \mu \text{m} \) of only 52.34 vs. 85.28 for NH\textsubscript{4}SH.

Our synthetic index models seem to beat the single-component compositions for the deep cloud because they contain important short-wavelength absorption lacking in water ice, as well as significant and spectrally flat long-wavelength absorption lacking in NH\textsubscript{4}SH. Our synthetic models seem to simulate the effects of combining both water ice and NH\textsubscript{4}SH, which suggests that the real deep cloud is some combination of these two materials, possibly a coating of NH\textsubscript{4}SH on top of water ice, or possibly a water cloud layer underneath a layer of NH\textsubscript{4}SH particles. In the left column of Fig. 20 it appears that the deep layer might have NH\textsubscript{4}SH as the dominant component, while in the right column perhaps H\textsubscript{2}O dominates. However, our attempts to fit the spectra with these two layers in close proximity did not even reach the fit quality achieved with single-layer models. The problem seems to be mainly in the wavelength region between 1 and 1.5 \( \mu \text{m} \). More work is needed in finding combinations of these two substances. Coated particles are prohibitively costly in computation time for the large particle sizes that seem to be required in this layer.

Changing the deep cloud model composition does have an effect on other parameters in the fit, as displayed in Table 4. For a deep cloud composed of only NH\textsubscript{4}SH, blocking thermal radiation from the deep atmosphere requires a much larger optical depth of layer 4 than is needed by a deep cloud of water vapor because of the latter’s more significant imaginary index. The pressures of most layers do not vary much for different models, with the exception of the pressure of the ammonia layer (layer 3) for fits to the eye spectrum with a deep layer composition of NH\textsubscript{4}SH, which is a low 0.71 bar compared to 0.82 and 0.88 bars for...
the other models. That model also has deviant values for particle radii. The fits to the 2013-Location 5 spectrum (left 4 columns in Fig. 20) show generally much less variability due to differences in deep layer models (with the exception of the optical depth of the deep layer for NH$_3$SH). There are also significant differences in the retrieved chromophore parameters. The resultant differences in wavelength dependence of refractive index components are shown in Fig. 21. The outlier for the 2013 fits is the model in which the bottom layer is pure water ice, in imaginary index (blue dot-dash curve) as well as in $\chi^2$. The outlier for the 2016 fits is the model in which the bottom layer is made of pure NH$_3$SH, also both in imaginary index (red dot-dash curve) and in $\chi^2$.

4.6. Vertical location of Saturn’s chromophore.

Karkoschka and Tomasko (2005) used HST observations to make a strong case for absorption of shortwave light in the stratosphere, and were successful in modeling their observations with spherical particles of the same composition in both the stratosphere and upper troposphere. Pérez-Hoyos et al. (2005) also placed short wave absorbers in both layers. The analysis closest in temporal and spatial coverage to our observations, is that of Sanz-Requena et al. (2018), which is based on Cassini ISS observations of the north polar region in 2013. That analysis found extremely low shortwave absorption in the upper troposphere, and stronger absorption in the stratosphere, but with a much flatter spectral variation than found by Karkoschka and Tomasko (2005). Stratospheric absorption in the north polar stratosphere was also confirmed by the detection of a UV dark polar hexagon at 180 nm by the Cassini Ultraviolet Imaging Spectrometer (Prvor et al. 2019).

At early stages of the modeling, we placed the chromophore in the stratosphere, with the top (stratospheric) layer of our model comprised entirely of chromophore particles. That worked reasonably well in fitting the observed VIMS spectra, but given the variability in prior results and the nature of our PH$_3$ retrievals, we also considered other options. The fact that our fits generally found a relatively rapid decline of PH$_3$ with altitude above the putative diphosphine cloud suggested that the stratospheric haze might not be providing much protection against the destruction of PH$_3$ by solar UV light. Another finding, i.e. that the putative diphosphine cloud did seem to provide that protection, suggested that diphosphine itself might be the chromophore, placing it well below the stratosphere. That model would reduce the attenuation of longwave UV light above that cloud, promoting the destruction of PH$_3$ above it, which seemed more compatible with our PH$_3$ results, although this ignores the important role of eddy mixing in controlling the PH$_3$ profile. More evidence on this topic is provided by the Braude et al. (2019) analysis of VLT/MUSE 480-930 nm spectra, which placed the chromophore within or just above the tropospheric haze, although their rather long short-wavelength limit of 480 nm might make them less able to constrain stratospheric contributions. If our layer 2 is actually composed of diphosphine and does not act as the chromophore at wavelengths longer than 0.35 $\mu$m, it would still absorb significant amounts of UV radiation up to $\sim$260 nm (Ferris and Benson 1981), and thus would still provide considerable protection against PH$_3$ destruction. Although the VIMS observations do not extend to wavelengths below 350 nm, and thus cannot directly constrain the degree of UV protection provided by either stratospheric or upper tropospheric layers, they do have the potential to constrain the location of the color-producing absorber. In the following subsection we describe our attempt.

![Fig. 19](image-url)

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Fig. 19.— Imaginary refractive index (A) and real index (B) spectra for candidate cloud particle compositions of NH$_3$SH (Howett et al. 2007), NH$_3$ (Martonchik et al. 1984), and H$_2$O (Warren 1984), compared to empirical deep cloud models (green curves). The dashed purple line displays a typical imaginary index model for the stratospheric haze layer that is the assumed source of Saturn’s tan color (its chromophore layer), computed using Eqns. 2-4 using $n_i$, $n_{i+1}$, $\lambda_1 = 0.35 \mu$m, $K_1 = 6.0$, $K_2 = 20$, and $\Delta = 0.11 \mu$m.
to constrain these possibilities using VIMS observation to evaluate four alternative vertical distributions of the chromophore.

4.6.1. Fit results for alternative models of chromophore vertical distribution

To try to constrain the vertical location of the chromophore, we focused on four model structures: (A) a four-layer model with the chromophore in the stratosphere; (B) a four-layer model with the chromophore consisting of the particles in the putative diphosphine layer (our lack of knowledge of the optical properties of diphosphine makes it impossible to rule out this possibility); (C) a 5-layer model with a high stratospheric haze providing some shortwave absorption, but most of the color provided by a separate chromophore layer just above the putative diphosphine layer, and (D) a 4-layer model in which the compositions of Layer 1 and Layer 2 were identical, an assumption made by both Karkoschka and Tomasko (2005) and Sánchez-Lavega et al. (2020). These structures are illustrated in Fig. 22 with best-fit parameter values given in Table 5 (Spectral plots are not shown because the different model cases are difficult to distinguish visually.)

We did one set of fits for location 5 in 2013 (left four columns in Fig. 22 and Table 5) and another for location 6 in 2016 (right four columns in Fig. 22 and Table 5). For both spectra, the model with the worst fit quality is the 4-layer model that assumes that the putative diphosphine layer is entirely made of chromophore particles (Model B). The other three options, i.e. a 4-layer model with the chromophore in the stratosphere (Model A) or a 5-layer model with a chromophore layer just above the putative diphosphine layer (Model C), and a 4-layer model with chromophore in both Layer 1 and Layer 2 (Model D), provide comparable fit qualities, but very different chromophore properties, as listed in Table 5 and displayed in the spectral plot in Fig. 23.

4.6.2. Evaluation of alternative chromophore models
Placing the chromophore either within the putative diphosphine layer (Model B in Fig. 22) or as a separate layer just above the diphosphine layer (Model C), has the potential virtue of being more compatible with our findings regarding the vertical distribution of phosphine gas. That distribution is characterized by a deep mixing ratio, a pressure breakpoint, and above that breakpoint a rapid decline with altitude. If it cause UV radiation dissociates PH$_3$, putting the UV blocking chromophore close to the PH$_3$ breakpoint is plausible. That allows dissociation of PH$_3$ above the chromophore, and protects PH$_3$ below that layer. In fact, it seemed plausible that the chromophore is being created by the very UV photolysis that is breaking down the phosphine gas above that layer. However, the fit quality is worst for the case in which the chromophore is distributed throughout layer 2 (Model B). And, as noted earlier, P$_2$H$_3$ has significant UV absorption even without the longer wavelength absorption needed to serve as a chromophore to shape the visible spectrum. The fit qualities for the other two options (Models A and D) are significantly better and comparable to each other.

In the case of Model B (the chromophore being the constituent that makes up the putative diphosphine layer), it is also necessary to have a stratospheric layer that performs two spectral shaping functions: filling in the deep methane absorption bands as needed and absorbing some of the light reflected by the putative diphosphine layer. For this option the stratospheric layer is treated as a pseudo-gray layer, which means using a wavelength-independent imaginary index, which produces a useful amount of absorption at short wavelengths, while not absorbing too much light at longer wavelengths.

Model D above (the stratospheric and upper tropospheric layers composed of the same material, with the same wavelength-dependent refractive index) is not attractive if diphosphine is the material, because it is hard to conceive of a diphosphine layer created in the stratosphere, where the phosphine abundance is expected to be vanishingly small.

A problem with placing the chromophore entirely within layer 2 (Model B) or at the top of layer 2
(Model C) is that the imaginary index required for the chromophore then becomes extremely large, reaching peak values exceeding 1.0, with accompanying large variations in the real index, as illustrated in Fig. 23. Even more extreme values are needed outside the hexagon for the 5-layer model. The other problem is that Karkoschka and Tomasko (2005), using HST imaging observations covering a wide range of filter peak wavelengths from 0.23 µm to 2.37 µm, established that the stratospheric haze contained aerosols with significant UV absorption. Their HST-based stratospheric haze index model, also shown in Fig. 23, has a spectral slope similar to our stratospheric model, but does not show a peak below 0.4 µm, instead continuing upward to rather large values at their shortest wavelength. However, the imaginary index variation they inferred is for an assumed constant real index, which violates the Kramers-Kronig relation. Another difference from our modeling is that they assumed the same refractive index model for tropospheric particles and...
as for the stratosphere and adopted a fixed radius of 0.08 μm, while we allowed that parameter to adjust as needed to improve the fit. Inside the hexagon we found aerosol radii from 0.06 μm to 0.12 μm in 2013, when optical depths were very low, and a nearly uniform radius of 0.2 μm in 2016, when optical depths were much larger. It is not clear to what degree these differences in analysis can account for differences in the inferred stratospheric refractive index. However, it is worth noting that the refractive index model provided in supplemental material associated with the Sánchez-Lavega et al. (2020) paper, which is based on an analysis of nadir HST observations, and also assumed the same index for stratospheric and tropospheric particles, did find a peak in the imaginary index near 0.4 μm, also shown in Fig. 23.

An additional problem with placing the main chromophore absorber in or at the top of Layer 2 is that there are more parameters to constrain, including the assumed wavelength-independent imaginary index of the stratosphere and the additional optical depth of the overlying layer (2C in the table). The result is increased uncertainty in the chromophore parameters, without providing an overall improvement of fit quality. Although we cannot rule out a vertically distributed chromophore, the least extreme and most convenient choice for modeling was to put the chromophore into the stratosphere.

### 4.7. Sensitivity of spectra to model parameters

The degree to which model parameters can be constrained by model spectra is illustrated by logarithmic derivative spectra in Fig. 24. These spectra were computed by perturbing each model parameter one at a time, then computing the fractional change in the model spectrum divided by the fractional change in the model parameter. The reference model for these calculations is for location 6 in 2016. The derivative spectra take the form

\[
\frac{\partial \log(I(\lambda; x_1, \ldots, x_N))}{\partial x_i} = \frac{(1/I)\partial I(\lambda; x_1, \ldots, x_N)}{(1/x_i)\partial x_i},
\]

where \(I(\lambda; x_1, \ldots, x_N)\) is the model spectrum for all parameters \(x_1, \ldots, x_N\) at wavelength \(\lambda\).
where $x_i$ is any of the model parameters $x_1, \ldots, x_N$, and $I$ is the model spectral radiance for the given set of parameters. The relation also holds if radiance $I$ is replaced by reflectivity $I/F$. The utility of these derivatives is that they have a simple interpretation. For example, panel E shows that a 1% increase in the effective stratospheric haze pressure will produce a 10% decrease in $I/F$ at 3.25 $\mu$m, a 3% decrease at 2.3 $\mu$m, but only a 1% decrease at 0.89 $\mu$m. Thus, it is apparent that the near-IR $I/F$ spectrum provides much stronger constraints on stratospheric haze vertical location ($p_2$) than do visible or CCD spectra. The vertical location of the second layer (the putative diphosphine layer at base pressure $p_2$) is also best constrained by the near-IR spectra, but different key wavelengths are involved. The parameters $p_1$ and $p_2$ have different spectral derivative signatures and are relatively uncorrelated.

A second way to assess the sensitivity of spectra to model structural parameters is illustrated in Fig. 25 which displays in the top panel a best fit model spectrum (solid black curve) along with spectra for models with layers removed (1, 3, 4) or halved in optical depth (2), all changes taken one at a time. Note that the dip near 2.9 $\mu$m is removed when the NH$_3$ ice cloud is removed (layer 3). Further note that the deep layer (4) only has significant spectral effects at short wavelengths, where CH$_4$ absorption is negligible, and at thermal emission wavelengths, where CH$_3$ absorption is also negligible. However, if the deep layer is replaced by particles with the same scattering parameters, but with a unit single scattering albedo, discrepancies then appear in the pseudo continuum regions with low methane absorption between 0.9 and 1.5 $\mu$m.

Also shown in the top panel is a model spectrum with the emitted contribution turned off (blue curve), showing the dominance of Saturn’s thermal emission to the spectrum at wavelengths beyond 4.5 $\mu$m. In the bottom panel are ratio plots of perturbed spectra to the best-fit spectrum, where the perturbations are to the main variable gases PH$_3$ and AsH$_3$.

### 4.8. Sensitivity of fits to initial guesses

Physical insight, guided by the logarithmic derivative spectra, was used to formulate initial guesses that provide at least crude fits to the observed spectra, which were then refined by our L-M algorithm. To see how sensitive the final results were to the initial crude estimates, we did some trial perturbed calculations, samples of which are illustrated in Fig. 26. Three fits are shown here, with initial guess and best-fit parameter values plotted for each case, shown as ratios to the parameter values obtained from the first best fit. The initial guess values for each case are plotted using gray filled circles. The best fit values for the first case are plotted as black dots with error bars. These all have unit central values because they have a unit ratio to themselves. The other fit results used initial values that were perturbed by either multiplying or dividing by 1.4. In the first alternative fit, the perturbations were in alternating directions, while they were all in the same direction in the second alternate. The resulting best fits using that guess, shown by open circles, were very close to the initial fit values, all well within the fitting uncertainties. We conclude that the fits are not very easily perturbed, indicating that there is no nearby fit that is better than the one we obtained.

## 5. FIT RESULTS

### 5.1. Overview of latitude-dependent vertical structure fits
Fig. 24.— Logarithmic derivative spectra for pressures (A-D), optical depths (E-H), particle radii (I-L), minor gas parameters (M-O), and chromophore refractive index parameters (P-R). See Table 3 and Eqns. 2-4 for definitions of variable names.
The results of fitting VIMS combined visual and near-IR spectra of the background clouds in the north polar region are summarized in Table 6 for 2013 and Table 7 for 2016. Both tables contain results from ten locations that avoid bright discrete cloud features. A sampling of the spectral fit quality for mid hexagon and eye regions for both years is provided in Fig. 27. The best-fit parameters and their uncertainties are compared in side-by-side plots versus latitude in Fig. 28. Fig. 29 provides an alternative set of plots that makes it easier to appreciate the evolutionary changes between 2013 and 2016. Similar comparison plots versus latitude of the column mass densities and their estimated uncertainties are presented in Fig. 30.

In general the pressures of the four layers are reasonably well constrained by the observations and do not vary dramatically with latitude except near the eye boundary in 2016. This stability of pressure levels is consistent with the aerosols being formed from condensates, but do not compel that conclusion. The biggest variation with latitude is in the optical depths of model layers in 2013, for which optical depths in-
inside the hexagon were substantially lower, decreasing by a factor of 4 to 5 relative to those outside the hexagon, with small additional decreases inside the eye region. In 2016 there was gradient of descent near the eye in the two middle layers, as their base pressures increased and optical depths dropped sharply inside the eye, to levels that are similar to those present over most of the region interior to the hexagon in 2013. One could roughly characterize the entire region inside the hexagon in 2013 as having an aerosol structure similar to that of the eye, but brightening substantially by 2016, leaving only the eye as a remnant. The increased optical depths of aerosol layers inside the hexagon by 2016 also contributed to the color change, which was further aided by increased absorption of blue light by the stratospheric haze as its imaginary index at short wavelengths increased as well as its optical depth.

5.2. Aerosol structure results by layer

Layer 1 (stratosphere). — The stratospheric haze parameters are best summarized in the right column of Fig. 29, which displays results for 2013 in blue and for 2016 in red. In 2013, the effective pressure of this layer is roughly in the 15 mbar to 50 mbar range. Uncertainties in effective pressure are so large that a clear trend with latitude is hard to discern in the 2013 results. There seems to be a descending trend towards the pole in 2016, but that is also uncertain. The optical depth trends are much better established. In 2016 the 1-μm optical depth of the stratospheric haze is near 0.2 from just south of the hexagon to just outside the eye, at which point it begins a rapid drop by a factor of five, to a value of 0.04, just twice the level seen in 2013 at the same location. But outside the eye, out to the edge of the hexagon, the 2013 optical depth of this layer remains near 0.04, about five times below the value found in 2016. The large increase in optical depth of the stratospheric haze between 2013 and 2016 is a major factor in changing the color of the region interior to the hexagon because that layer is a strong absorber of blue light, as evident from the fitted imaginary index model displayed in panel E of the right column of Fig. 29. Increased absorption in 2016 was further aided by an increase in the imaginary index by about a factor of 3 between 2013 and 2016. This indicates that the stratospheric haze particles are not of uniform composition. One possibility is that they are a mixture of two components, and the fraction of the short-wave absorber component is increased over time by UV photolysis. A more complex changing composition is also possible. Two parameters of the imaginary index that did not change significantly between 2013 and 2016 are the log slope parameter $K_1$, which averaged 5 to 6 at both times, and the wavelength of the peak, which remained near 0.35 μm during both periods. It is also noteworthy that the best fit chromophore index models in the eye region for the two years are much more similar than the mid-hexagon values. In 2013 the particle radius for this layer was roughly 0.05 μm inside the hexagon with perhaps a decrease inside the eye, though uncer-
Layer 2 (putative diphasic layer). — This layer remained very close to a latitude independent pressure near 300 mbar for both 2013 and 2016, with one exception, that being in the eye region in 2016 for which it descended to a pressure near 590 mbar. A different story is told by the optical depth of this layer. In 2013 it declined from 1-2 outside the hexagon to one tenth that value inside the eye, with a decline that was distributed over latitude rather than marked by sharp changes. In 2016, however, the optical depth of this layer reached 3 outside the hexagon and remained above 1.0 out to the edge of the eye, at which point it sharply dropped to the level it had in 2013. The particle radius for particles in this layer in 2016 was essentially independent of latitude at about 0.5 µm from just south of the hexagon all the way to the edge of the eye, at which point it dropped to just above 0.1 µm inside the eye. Between 2013 and 2016 the mid-hexagon column mass density for this layer actually did increase by a factor of two, as might be expected from the large increase in optical thickness. In 2013 its particle radius was ~0.3 µm from outside the hexagon to 76°N, but stayed near 2 µm from 78°N almost to the edge of the eye at 88.8°N (except for the increase at Location 2, which has an unusually high optical depth in the upper atmosphere).

Layer 3 (NH3 ice). — This layer in 2013 was at nearly constant pressure near 900 mbar inside the hexagon,
rising just slightly (to a lower pressure near 630 mbar) at the edge of the hexagon. In 2016 however, there was a rise in altitude with latitude, moving from 1 bar just outside the hexagon to 520 mbar at the edge of the eye, but inside the eye the layer dropped in altitude to a pressure near 1 bar again. In 2013 the optical depth inside the hexagon was fairly flat at about 0.1, rising at the edge of the hexagon and at the edge of the eye to values near 1.0, a factor of 10 increase, but dropped sharply inside the eye, to 0.025. In 2016 the layer dropped in altitude to about 12 µm was followed by a decline with increasing latitude to about 4 µm. This large layer-3 particle size for location 2 is somewhat of an anomaly, which is discussed in Sec. 6.1.

Layer 4 (NH₃ + H₂O + ?). — The base pressure of this layer ranged from 2.7 to 4.5 bars, with most of the fits close to 3.3 bars. The pressures are well defined because of their strong effect on emitted radiation. The optical depths retrieved for this layer have been between 2 and 7, with particle sizes ranging from about 20 to 30 µm, although the higher numbers are not well constrained. Exceptions are seen at the eye, where optical depths seem to be too large to allow defining an upper limit. These results are for an assumed real index of 1.6, which is between that of water ice and NH₃, and for an imaginary index profile displayed in Fig. 19 which has in a very crude sense the wavelength dependence of a mix of water ice and NH₃, but of a higher magnitude. The need for extra

| Locations: | 10 | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 | 1 |
|------------|---|---|---|---|---|---|---|---|---|---|
| Parameter \ Lat. | 72.6° | 75.0° | 76.0° | 80.0° | 83.1° | 85.6° | 87.4° | 88.2° | 89.0° | 89.6° |
| $p_1$ (bars) | 1.5±1.0 | 1.7±1.5 | 2.7±3.9 | 2.9±5.1 | 3.1±5.0 | 4.4±4.3 | 5.1±4.1 | 1.9±1.4 | 4.7±1.0 | 5.6±1.5 |
| $p_2$ (bars) | 3.0±0.1 | 3.0±0.1 | 3.0±0.1 | 3.0±0.1 | 3.0±0.1 | 3.0±0.1 | 3.0±0.1 | 3.0±0.1 | 3.0±0.1 | 3.0±0.1 |
| $p_3$ (bars) | 10.7±1.2 | 8.3±0.5 | 7.2±0.4 | 6.9±0.4 | 6.1±0.4 | 5.9±0.4 | 5.8±0.5 | 5.8±0.5 | 5.8±0.5 | 5.8±0.5 |
| $p_4$ (bars) | 3.4±0.2 | 2.8±0.2 | 2.4±0.3 | 2.1±0.3 | 2.0±0.3 | 2.0±0.3 | 2.0±0.3 | 2.0±0.3 | 2.0±0.3 | 2.0±0.3 |

| $r_1$ (µm) | 2.18±1.7 | 2.12±1.9 | 2.03±1.7 | 2.18±1.7 | 2.10±1.7 | 1.92±1.9 | 1.85±1.6 | 8.4±1.6 | 5.4±1.8 | 4.0±0.8 |
| $r_2$ (µm) | 9.4±0.1 | 4.9±0.1 | 4.7±0.1 | 4.8±0.1 | 4.9±0.1 | 4.9±0.1 | 4.9±0.1 | 4.0±0.1 | 2.6±0.2 | 2.0±0.3 |
| $r_3$ (µm) | 2.0±0.7 | 1.9±0.4 | 1.6±0.2 | 1.8±0.3 | 1.9±0.3 | 2.1±0.3 | 3.0±0.5 | 3.0±0.5 | 3.0±0.5 | 3.0±0.5 |
| $r_4$ (µm) | 45 | 36.5±6.7 | 45.0±0.0 | 45.0±0.0 | 18.6±6.5 | 18.0±6.5 | 18.0±6.5 | 43.8±12.2 | 7.8±2.0 | 13.3±4.3 |
| $r_1$ (µm) | 25.4±3.6 | 27.5±3.6 | 28.7±3.6 | 29.9±3.6 | 31.1±3.6 | 32.3±3.6 | 33.5±3.6 | 34.7±3.6 | 35.9±3.6 | 37.1±3.6 |
| $r_2$ (µm) | 32.9±3.2 | 24.3±3.2 | 19.4±3.2 | 14.9±3.2 | 10.4±3.2 | 6.9±3.2 | 3.4±3.2 | 1.9±3.2 | 1.0±3.2 |
| $r_3$ (µm) | 9.4±2.2 | 1.8±0.8 | 6.9±0.8 | 5.9±0.6 | 4.7±0.6 | 4.1±0.6 | 2.2±0.3 | 1.7±0.3 |
| $r_4$ (µm) | 5.6±1.9 | 6.9±2.4 | 3.1±1.3 | 5.7±1.6 | 4.0±0.8 | 3.0±0.9 | 6.7±3.0 | 6.1±5.0 |

$\chi^2$ = 395.45
$\chi^2/N_{DF}$ = 1.54

TABLE 7

Best-fit model parameters as constrained by 2016 observations.

NOTE: Here location numbers refer to encircled pixels shown in Figs. 6.8 and 15.1. Optical depths are given at a wavelength of 1 µm. Reflective index values for each aerosol layer are discussed in the text. Fixed values and computational details are as described for Table 6. Meaningful uncertainties for $r_4$ and $M_4$ for location 10 were not possible because the best fit value of $r_4$ reached the upper limit of our allowed range.
absorption in this layer, beyond that provided by pure NH₃SH or water ice, was also noted by Barstow et al. (2016) and Sromovsky et al. (2020a).

Aerosol column mass densities. — The column mass densities from Tables 6 and 7 are compared in Fig. 30 as a function of latitude. The stratospheric haze layer is surprising in two respects: first, its column mass density is comparable to that of layer 2, even though its optical depth is 4-10 times smaller, and second, its increase in optical depth from 2013 to 2016 is accompanied by a decrease in column mass density rather than the expected increase. A possible cause is that increased photochemical production of stratospheric condensables in 2016 results in more condensation on existing nuclei, which increase in size and fall faster to a level where they evaporate, taking more mass out of the layer, but still serving to increase the effective particle size in the stratosphere enough to produce an increase in optical depth because of greatly increased scattering efficiency. This scenario would suggest that the bottom of the stratospheric haze would need to be at pressures exceeding 100 mbar. Particles above that level and falling to higher pressures would experience decreasing temperatures as they fell and thus would not evaporate before that level. The actual situation appears to be much more complicated, given the evidence of multiple compact haze layers in limb observations (Sánchez-Lavega et al. 2020). The column mass density of the putative diphosphine layer (layer 2) did increase between 2013 and 2016, while its particle size changed very little. The ammonia ice layer column mass density generally increased over time but displayed some large deviations, most notably for location 2 in 2013, which was roughly two orders of magnitude more massive than its neighboring locations, along with its much larger particle size and optical depth. The cloud structure in Location 2 is dominated by the ammonia ice layer and further discussed in Section 6.1. Layer 4 is the most massive (note that M₄ is given in mg/cm² instead of µg/cm²) but more variable with latitude.

5.3. Minor gas fit results

Ammonia. — The VIMS north polar spectra are somewhat sensitive to the volume mixing ratio of ammonia in the depleted region above the 4-bar level. The greatest sensitivity was obtained for observations in 2013, when overlying aerosol opacity was lower than in 2016. Fig. 31 indicates that the depleted-region VMR in 2013 (blue dotted line) was relatively independent of latitude from 76°N (just inside the hex boundary) all the way to the eye, with a mean value over that region of 50.5±6 ppm, with a standard deviation of 16 ppm. This is comparable to the lowest value (at 10°S) inferred by Fletcher et al. (2011b) for their 2-cloud scattering model of aerosols. Their more typical values in the northern hemisphere, up to 65°N, were about double that value, with higher
values near the equator, indicative of upwelling motions there. (The Barstow et al. (2016) reanalysis of the nightside VIMS observations used by Fletcher et al. found about twice their levels of NH₃.) Our lower 2013 values in the north polar region, even lower than the 70-110 ppm depleted values of Briggs and Sackett (1989), are indicative of downwelling motions. However, our results for 2016 favor much lower values, although these are very uncertain because of the obscuring effects of increased aerosol optical depths. The upper limits of the uncertainty range for these values can reach almost to the 2013 levels in some cases. Just outside the hexagon both 2013 and 2016 values are low and comparable, but also with greater uncertainty because of high aerosol optical depths in that location for both years. The suggested downwelling in regions of increased aerosol opacity is hard to understand. The alternative interpretation, i.e. that the retrievals are biased by the aerosol obscuration, cannot be entirely ruled out. One feature of our 2013 retrievals that seems at least qualitatively consistent with 2015 microwave observations at the Very Large Array is a local depletion of the NH₃ abundance at the outer boundary of the hexagon (Li et al. 2020). However, the VIMS results closest in time (for 2016) do not agree with relative variation with latitude indicated by the VLA results, casting further doubt on the large depletions found near the hexagon boundary in our 2013 retrievals.

**Arsine.** — Our results for AsH₃ are relatively simple. Its VMR is about 2 ppb and displays only small variations with latitude and time (see Fig. 31C). Between latitudes 72°N and 90° N we found mean values of 2.18±0.19 ppb in 2013 and 1.76±0.08 ppb in 2016, with standard deviations of 0.54 ppb and 0.24 ppb respectively. Individual measurement errors were typically about 0.5 ppb. The increased mean value for 2013 was mainly due to increased values derived in regions of low aerosol opacity, suggesting that the arsine mixing ratio declines with altitude above the cloud level, although this is not very dra-
sults of Bézard et al. (1989) who derived $\text{AsH}_3$ mixing ratios of $2.4^{+1.1}_{-0.5}$ ppb for what they call the thermal component and $0.39^{+0.23}_{-0.1}$ ppb for what they refer to as the reflected solar component. The latter is probably representative of their effective value above the 200 – 400 mbar range where they inferred a haze layer, while the former applies to the deep mixing ratio. Our result for 2016 is comparable to the $1.8^{+0.1}_{-0.1}$ ppb found for the south polar region between $71^\circ$S and $86^\circ$S by Sromovsky et al. (2020a), which is derived from VIMS day-side near-IR spectra. Our 2013 result is a close match to the Fletcher et al. (2011a) global value of $2.2^{+0.3}_{-0.1}$ ppb, obtained from nighttime VIMS observations, but our 2016 value is in slight disagreement. Both results are lower than the less accurate global estimate of $3^{+1}_{-1}$ ppb by Noll et al. (1990).

**Phosphine.** — Our results for $\text{PH}_3$ are displayed in Fig. 31B and C. The deep mixing ratio seems to have very little latitudinal variation outside the eye. Between $72^\circ$N and $88^\circ$N, we found mean values of $5.30^{+0.3}_{-0.2}$ ppm in 2013 and $4.74^{+0.1}_{-0.1}$ ppm in 2016, with standard deviations of 0.71 ppm and 0.28 ppm respectively. These are somewhat larger than the 4.4 ppm (std. dev. 0.2 ppm) found for background clouds in the south polar region (Sromovsky et al. 2020a), but well below the 6 ppm we estimated by averaging the 2007 CIRS-based results of Fletcher et al. (2008) over a similar northern latitude range. We also found no evidence of their inferred decrease in VMR from 7.4 ppm at $88^\circ$N to 4.8 ppm at $90^\circ$N. Instead we see almost the exact opposite in our 2016 results: an increase from $4.8^{+0.5}_{-0.5}$ ppm at $88^\circ$N to about $7.5^{+0.5}_{-0.5}$ ppm near the pole. This discrepancy might be due to differences in how the $\text{PH}_3$ profile was parameterized, or possibly a temporal variation. A much smaller latitudinal variation is indicated in our 2013 results: just a 1 ppm increase over a similar latitude interval, which is almost consistent with no increase. Global average results of Orton et al. (2009), corrected by Orton et al. (2001), are consistent with a deep $\text{PH}_3$ VMR of 7.4 ppm, which is also consistent with the $7^{+3}_{-2}$ ppm deep value derived by Noll and Larson (1991) from analysis of Saturn’s 4.5–5 $\mu$m spectrum measured in 1981. The two analyses of the same VIMS nightside observations disagreed about the $\text{PH}_3$ VMR values. Except for a local minimum near the equator, Fletcher et al. (2011a) retrieved values near 3 ppm, almost independent of latitude for their scattering cloud model, while Barstow et al. (2016) retrieved values about twice as large, and ranged between 4 ppm and 6 ppm in the northern hemisphere. Our results would seem to be in better agreement with Barstow et al. (2016), although neither of the two nightside analyses covered the polar region that we observed.

What we found to be most variable in the $\text{PH}_3$ profile is the breakpoint pressure, which largely followed the effective pressure of the main cloud layer except where its optical depth decreased to just a few tenths, at which point the breakpoint pressure increased dramatically. This is well illustrated by the difference
between 2013 and 2016 results displayed in Fig. 31B. This shows that the PH₃ breakpoint pressure for 2016 is almost exactly equal to the base pressure of aerosol layer 2, which outside the eye has an optical depth greater than 1.0. But inside the eye that layer’s optical depth declines dramatically, which is accompanied by a sharp increase in the breakpoint pressure. In 2013, layer 2 reaches optical depths greater than one only outside the hexagon, where the breakpoint pressure again matches that layer’s base pressure. But inside the hexagon in 2013 the optical depth of layer 2 declines by a factor of 10, resulting in the breakpoint pressure increasing beyond the base pressure of the ammonia cloud (layer 3). This behavior is consistent with the idea that the upper tropospheric cloud layer is shielding the vertically mixed PH₃ from destruction by incident solar UV light, as discussed in review chapters by Fouchet et al. (2009) and Fletcher et al. (2019).

Our models are generally consistent with a steep decline in the PH₃ VMR above the relatively thick cloud layers. However, an exception occurs in regions with high optical depths in the ammonia layer, such as the 2013 location 2 and location 11, where the breakpoint seems to occur at much lower pressures (see discussion in Sec. 6.1). It should also be noted that the chromophore, which we assume to be in the stratosphere, should also provide protection, but has such a low optical depth that it only absorbs a modest fraction of the UV light. Furthermore, we cannot be sure that the chromophore particles remain strong absorbers at wavelengths much below the 350-nm lower limit of the VIMS observations, which might further reduce protection by the stratospheric layer. Although we assumed no UV absorption in our modeling of the putative diphosphine layer, if that layer is actually composed of diphosphine, it would block UV light at wavelengths below the lower limit of VIMS observations, as already noted, in which case there indeed would be protection provided by that layer.

5.4. Changes in cloud structure between 2013 and 2016

Another way to look at changes in aerosol structure is provided in Fig. 31 which displays model structures for three typical regions for 2013 and 2016 side by side. Just outside the hexagon the most significant change is in the optical depth of the putative diphosphine layer, which increases from 1.25 to 3.31. The main change in the stratospheric haze is the increase in particle radius from 0.13 µm to 0.22 µm. Inside the hexagon there are significant changes in both the stratosphere and the deeper layers. The stratospheric haze particle size doubled and the optical depth increased by a factor of four. The putative diphosphine layer experienced similar changes, while the main change in the ammonia layer was a nearly tripling of the optical depth and a nearly 300 mbar decrease in pressure. Inside the eye region there was a doubling of the optical depth of the stratospheric haze up to a still small value of 0.05, with little change in particle size, and a small 30 mbar increase in pressure. There were also substantial changes in the deep cloud layer, but these are likely due to different sampling of significant deep spatial variations, temporal changes in that layer seem to occur with a speed not characteristic of slow seasonal changes.

5.5. The nature of the north polar transformation

Spectra from the middle of the hexagon region are shown in Fig. 33A for 2013 and 2016, along with their computed colors. Although the spectra are dramatically different, the color differences are more subtle, with 2013 being somewhat greenish blue and 2016 being somewhat gold. At longer wavelengths, where Rayleigh scattering contributes much less and methane absorption becomes more significant, the 2016 I/F becomes many times as large as seen in 2013. But these large differences don’t affect visual color very much.

To better understand how aerosol changes created these spectral differences, we show in Fig. 33B the effect of replacing 2013 model components with 2016 model components. We begin with the 2013 model structure with its corresponding spectrum recomputed for the observing geometry of 2016, which is shown as the black curve. The blue-green color is brightened at this observing geometry due to more favorable illumination, which especially brightens the shortest wavelengths. By replacing layer 1 of the 2013 model with layer 1 of the 2016 model, this excess short-wavelength brightness is almost entirely eliminated and the color is transformed to what is essentially identical to the color of the complete 2016 model. Thus the visual color change from 2013 to 2016 can be entirely attributed to changes in the stratospheric layer. According to Tables 6 and 7, the main changes in this layer included particle radius increase from 0.09±0.015 µm to 0.21±0.02 µm, an optical depth increase from 0.05±0.01 to 0.19±0.03, and an important increase in the imaginary index peak from 0.06±0.01 to 0.17±0.06. The wavelength peak and log slope of the imaginary index did not change significantly. The change in the peak amplitude suggests a compositional change, or a change in the fraction of haze particles of fixed composition relative to a non-absorbing component that was present in 2013 but not increased by photolysis over the three-year interval. The increase in particle radius by a factor of 2.3 and the increase in optical depth by a factor of 3.8, strangely does not seem to imply a column mass increase. Although highly uncertain for the small particles in the stratospheric layer, the calculated mass densities given in Tables 6 and 7 actually indicate a column mass decrease as the optical depth of the stratospheric layer increased. Perhaps this is an indication that the extinction efficiency of stratospheric particles has a size dependence different from that of spherical particles. The other effect produced by the changes in the stratosphere was the increase in I/F in the deep methane absorption bands. This was mainly due to increased scattering rather than the very slight
That layer’s particle size decreased slightly, with continuum I/F values (as evident from the red curve in Fig. 33B) also had the effect of filling in the PH₃ absorption bands, most notably the 4.3-μm band. That means that the PH₃ pressure breakpoint had to move from 1.12±0.09 bars to 0.28±0.02 bars. The change in the ammonia layer (layer 3) provided the remaining boost needed in the pseudo-continuum I/F values (as evident from the red curve in Fig. 33B). That layer’s particle size decreased slightly, from 3.0±0.4 μm to 1.9±0.3 μm, while its optical depth increased from 1.7±0.1 to 4.9±0.6. The changes in the deep layer had little effect on the external spectrum. And the change in the AsH₃ amount was inside the error bars.

The changes in the structure of the eye region between 2013 and 2016 are much more subtle, with very little difference in the optical depths of the top two layers that are most responsible for the visual color of the region, as evident from Fig. 28. The color change that is observed is mostly due to changes in the observing geometry, as evident from the model spectra displayed in Fig. 34.

Outside the hexagon, model spectra in Fig. 35 show that the change in viewing geometry has a negligible effect on the visual spectrum, with the substantial color shift from yellow-green to gold, produced by increases in stratospheric haze absorption, as shown in Fig. 28.

6. DISCUSSION

6.1. Cloud features with strong NH₃ ice signatures

Although we intended to avoid discrete bright clouds in this study, at location 2 in the 2013 VIMS observations we happened to sample a circular band of clouds with an unusual spectrum having a large ratio of I/F at 2.7 μm to that at 3.05 μm. Our fit to that spectrum produced an ammonia ice layer with unusually large particles (12 μm instead of the more typical 2-3 μm) and an unusually large optical depth (0.8 vs 0.1-0.2 for mid hexagon clouds). To illustrate how well the composition of that layer is constrained by the observations, we tried fitting that layer with three different compositions, all with the po set to 0.05 bar: ammonia ice, NH₄SH, and a fixed real refractive index of 1.4 and zero imaginary index. The best fits with those compositions yielded χ² values of 322.94, 371.48, and 410.10, respectively, clearly indicating a strong model preference for ammonia ice as the composition of layer 3. This is so obvious because in this case the ammonia ice layer is not obscured very much by the overlying aerosols that here have only about 1/9 the optical depth. For most of the background cloud structures, the overlying layers have about twice the optical depth of the ammonia ice layer, which makes its composition far less detectable.

Fitting the PH₃ pressure breakpoint for location 2 also produced an anomalous result. Instead of finding a value near 1.5 bars, as found just south of the feature, the fitted value was driven to the lowest value in our fit range. By doing additional fits at fixed values of po from 0.01 bar to 0.5 bars, we discovered that χ² is low and varies erratically up to about po = 1.5 bars, at which point it rises dramatically. Our initial automated fit apparently got stuck at the lower boundary of our fit range, because of the bumpy χ² terrain in
**Fig. 33.** — A: Model spectra in the middle of hexagon region in 2013 (black, from location 5 in Fig. 14 and Table 6) and 2016 (red, from location 5 in Fig. 15 and Table 7), with corresponding colors computed for each. The spectra are from locations 5 and 6 respectively from Figs. 14 and 15, at latitudes of 81.6°N and 83.1°N respectively. B: Transformation of 2013 model spectrum computed at 2016 observing geometry (black) by replacing layer 1 (dotted), by replacing layers 1 and 2 (dashed) and by replacing layers 1 and 2 and minor gas profiles (red), where replacement layers come from the 2016 model. This shows that most of the visual color change is due to the top layer, while most of the near-IR spectral change is due to layer 2. The numbers at the right of each color bar are RGB tristimulus values normalized by the white reference values.

**Fig. 34.** — A: Spectra inside the north polar eye in 2013 (black, from location 1 in Fig. 14 and Table 6), in 2016 (red, from location 1 in Fig. 15 and Table 7), and the 2013 model spectrum computed for the 2016 observing geometry (green). B: a logarithmic plot of results in A.
that region. Our subsequent series of fits shows that $p_0$ cannot be within 0.15 bars, which is at least ten times lower than for samples just south of location 2. This indicates that within the ring of clouds sampled by location 2 in 2013, there is an upwelling that lifts PH$_3$ to fairly low pressures. This upwelling might also be the origin of the enhanced optical depth of the ammonia cloud layer.

Another spectrum with a strong NH$_3$ ice signature is that for location 11 in 2013, as previously noted. Fitting our model structure to that spectrum, we find an even larger optical depth in the ammonia ice layer (2.5 vs 1) with a similarly low optical depth (0.23 vs 0.1) in the putative diphenylphosphine layer. We also found a high value for the PH$_3$ VMR (7 ppm versus the 5 ppm more generally retrieved). A more extensive analysis of NH$_3$-signature cloud features in the south polar region by Sromovsky et al. (2020a) also found an enhancement of the deep PH$_3$ VMR compared to values derived from background cloud spectra. Our assumed composition for layer 3 was also tested by fitting the same three alternatives used for the location 2 spectrum, with the following $\chi^2$ results: 394.47 (NH$_3$ ice), 1081.99 (NH$_4$SH), and 1468.82 (real index 1.4 and zero imaginary). In this case NH$_3$ ice is the overwhelmingly preferred composition for layer 3. In the two very poorly fitting cases, the main fit discrepancies appear near 2 $\mu$m, 3 $\mu$m, and 4 $\mu$m.

6.2. Is there enough PH$_3$ to make a cloud of P$_2$H$_4$ particles?

The plausibility of P$_2$H$_4$ as the composition of layer-2 cloud particles and photolysis of PH$_3$ as the source of those particles, depends in part on the available supply of PH$_3$. The idea is more plausible if the mass of the cloud does not exceed the mass of the PH$_3$ vapor within the cloud. The column density of PH$_3$ over a pressure interval of $\Delta P$ is given by $(M_{PH_3}/M)\alpha_{PH_3}\Delta P/g$, where $g$ is gravity (12.13 m/s$^2$ at 88°N), $\alpha_{PH_3}$ is the volume mixing ratio of PH$_3$ (about 5 ppm), and the ratio of molecular weights of PH$_3$ to the total is given by $34/2.2 = 15.45$. This evaluates to a column mass density of $6.4 \times 10^4$ $\mu$g/cm$^2$/bar, and for a layer thickness of 30 mbar would provide 1900 $\mu$g/cm$^2$ of PH$_3$ within the assumed thickness of the layer 2 cloud, which is about 300 times the column mass density of the cloud itself, and thus could provide about 150 times the number of phosphorous atoms needed to create the cloud particles. Thus a net upwelling flow of just 1/150th of the particle fall velocity could sustain the cloud mass density, making PH$_3$ a very plausible source of cloud material for layer 2. According to Fig. 11 of Roman et al. (2013), the fall speed of these particles (for $r = 0.2–0.3$ $\mu$m and $\rho \approx 0.8$ g/cm$^3$) should be about 0.02 – 0.1 mm/s, which converts to 1.8 – 9 km/year.

6.3. Is there enough local NH$_3$ to supply the inferred NH$_3$ cloud?

The small ammonia vapor mixing ratio we often find for the region above the breakpoint pressure raises questions about the viability of ammonia condensation as the source of particles in layer 3. Applying the analysis of the previous subsection to the ammonia cloud, assuming a local NH$_3$ mixing ratio of about 10 ppm, and a typical assumed layer thickness of about 90 mb we find an ammonia vapor mass density of 6386 $\mu$g/cm$^2$/bar, and thus about 576 $\mu$g/cm$^2$ within the cloud layer, which is 25-50 times the column mass density of particles, and thus could replenish that mass by an upwelling that was just 1/50th to 1/25th of the particle fall speed, which also makes ammonia a plausible constituent for layer 3, even at significantly lower mixing ratios, which is already plaun-
sible on other grounds, namely that where its optical thickness is significant, it actually displays obvious ammonia spectral features.

6.4. Could the chromophore be universal?

Although the spectral shape of our chromophore fits for 2013 and 2016 are very similar, the absolute levels of absorption in the chromophore particles as measured by the fitted imaginary index, is not constant. Although the imaginary index is fairly constant as a function of latitude for 2013, its absolute level outside the eye for 2016 is roughly a factor of three higher than the 2013 value. Karkoschka and Tomasko (2005) used a fixed spectral shape to fit all latitudes and years in their data set, but also had to significantly adjust the absolute level of absorption by a factor of ten between low and high latitudes. Thus, the inherent particle composition seems to vary, although this might be only an apparent characteristic arising from a mix of two component particle populations, one with a fixed composition that has a fixed absorption level mixed with a second component that is conservative. In this case it would be a varying ratio of two components rather than a variation in the composition of either component. This situation is unlike that observed for the chromophore on Jupiter, where Sromovsky et al. (2017) showed that a wide range of color variations can be well fit with a nearly universal chromophore with a single composition. The lack of a universal chromophore on Saturn is also suggested by the work of Braude et al. (2019), who concluded that two or more color-producing mechanisms were at work. We also made some trial calculations to further explore this issue. We tried to fit a 2016 spectrum with a chromophore derived from 2013 and found that the best-fit χ² minimum increased from 317.02 to 742.93, a huge worsening of the fit. Going in the opposite direction, we tried fitting a 2013 spectrum with a chromophore derived from a 2016 spectrum (which has a much larger imaginary index). In that case χ² increased from 281.46 to 312.13, still a significant worsening of the fit, but not as dramatically as for the previous case.

6.5. Can fit results apply to models with vertically extended layers?

Because the VIMS polar spectra are not strongly sensitive to the vertical extent of the cloud particles in each layer (as long as the base of each layer is not fixed), it is hard to constrain the eight additional parameters needed to define the extra boundary and the fractional scale height for the four layers in our standard model. We thus chose vertically thin particle layers to simplify the model so that fewer parameters would need to be constrained and the non-linear regression we used to retrieve parameter values would be more stable. Although we did not find a need for vertically extended layers to fit the spectra accurately, the spectra do allow such layers to be present, and in some cases such layers might be more appropriate. Thus it is worth considering how we might translate our thin layer results to models with more vertically extended layers. From trial calculations shown in Fig. 36 we found that very nearly the same fit quality can be obtained just by refitting the top and bottom cloud boundaries. We also found that fairly accurate approximations for the locations of the shifted cloud boundaries can be obtained by assuming that the average pressure of the cloud remains the same independent of the vertical extent of the cloud boundaries and independent of the particle scale height. Equations for that approximation are provided in the following.

The most general equation for the mean pressure depends on the top and bottom pressures and how the particles are distributed between them. Suppose an aerosol layer between pressures \( p_b \) and \( p_t \) has an optical depth \( \tau_{tot} \). Further suppose that the aerosol optical depth is vertically distributed with scale height \( H_a \) and that \( H_g \) is the gas (pressure) scale height. That distribution can be written as

\[
d\tau = \frac{\tau_{tot}}{f} \left( \frac{1}{p_b^{1/f}} - \frac{1}{p_t^{1/f}} \right) p^{1/f-1} dp
\]

where \( f = H_a / H_g \) is the aerosol to gas scale height ratio. The mean pressure within that layer can then be written as

\[
< p > = \int_{p_b}^{p_t} p d\tau(p) / \tau_{tot} = \frac{p_b}{1 + f} \left( \frac{1 - t^{1/f+1}}{1 - t^{1/f}} \right)
\]

where \( t = p_t / p_b \). This results in the following approximation for relating pressure boundaries for one set of \( f \) and \( t \) values, to those with a different set of values:

\[
\frac{p_{b2}}{p_{b1}} = \frac{p_{b1}}{p_{b2}} \left( \frac{1 + t_1}{1 + t_2} \right) \left( \frac{1 - t_1^{1/f+1}}{1 - t_2^{1/f+1}} \right) \left( \frac{1 - t_2^{1/f}}{1 - t_1^{1/f}} \right)
\]

\[
\frac{p_{t2}}{p_{t1}} = p_{t1} / p_{t2}
\]

where subscripts 1 and 2 refer to initial and final values respectively. These approximations are shown as red dashed curves in Fig. 36. In panel A of that figure all layers have \( f_1 = f_2 \), which reduces Eq. 2 to the much simpler form

\[
\frac{p_{b2}}{p_{b1}} = \frac{p_{b1}}{p_{b2}} \left( \frac{1 + t_1}{1 + t_2} \right)
\]

\[
\frac{p_{t2}}{p_{t1}} = p_{t1} / p_{t2}
\]

In that panel the plot of \( \chi^2 \) vs \( t \) indicates that somewhat better fits would have been obtained for this spectrum if we had used \( t = 0.6 \), instead of \( t = 0.9 \). Our results for the bottom pressures would then be increased by the ratio of 1.9/1.6 = 1.19 and our top pressures decreased by the factor 0.6 × 1.19 = 0.71. That would change the layer 2 boundaries from 252-280 mbar to 179-333 mbar, with the same mean of 266 mbar. Another conversion example is provided in Fig. 36. In this case we assumed a fixed value of \( t = 0.3 \) and varied the scale height ratio from 0.1 to 1.0. The \( \chi^2 \) plot indicates that aerosol layers vertically extended to this degree would have a small
6.6. Comparison with prior vertical structure models

A summary of the time and space sampling of selected published works on Saturn’s cloud structure covering the last Saturnian year (29.5 earth years) was previously displayed in Fig. 1. A rough depiction of the vertical structure models of these various works is presented in Fig. 37 in order of publication date. The temporal sampling and spatial coverage are indicated in tabular format at the top of the figure. Most of these are based on analysis of reflected sunlight in the CCD spectral range, which have very limited sensitivity to the deeper aerosol properties. Two (F2011 and B2016) are based on nightside VIMS observations of thermal emission in the 5-10 µm region, which have sensitivity to deep clouds, but very limited sensitivity to the stratospheric and upper tropospheric aerosols, and do not cover either polar region. One study (S2020) made use of VIMS near-IR dayside spectra of the south polar region, and used both reflected sunlight and thermal emission together to provide a wider range of vertical sensitivity. At the time of the previous overview of our understanding of Saturn’s aerosols by Fletcher et al. (2019), there was a consensus that seasonal insolation changes induce hemispheric asymmetries in the tropospheric (and likely stratospheric) hazes, with higher opacity in the summer hemisphere and lower opacity and a bluer visual color in the winter hemisphere. Consistent asymmetries were also observed at near-IR wavelengths, with increased upper tropospheric opacity producing greater attenuation of Saturn’s 5-10 µm emission in the summer hemisphere (Baines et al. 2006; Fletcher et al. 2011a). There has also been a consensus that that upper tropospheric aerosols reach to higher altitudes at the equator and stratospheric aerosols reach their greatest opacity in the polar regions. The work we present here (designated as S2021 in the aforementioned figures) is the only one based on simultaneous constraints of VIMS visual and near-IR spectra covering the 0.35-5.12 µm spectral range and also uses both reflected sunlight and thermal emission. In the following we first compare our north polar results with other models of the same region, and then we compare our results with south polar results.

6.6.1. North polar comparisons

Comparison to 1991 results.

Karkoschka and Tomasko (2005) derived pole to pole stratospheric and tropospheric aerosol properties from HST observations sampled from 1991 to 2004 (Fig. 1). Their model contains two uniformly mixed particle layers of the same composition but they allowed that composition to vary with time and latitude. Their top (stratospheric) layer extends upward from a fixed bottom pressure of 50 mbar and their bottom (tropospheric) layer extends downward below a variable top pressure. For the stratospheric layer, they chose a particle radius of 0.08 µm, independent

scale height ratio, probably less than 0.3. The boundary model approximation for this vertical distribution also matches pretty well the best fit values. Thus, Eq. 9 provides a general and reasonably accurate way to relate our results to models with more vertically extended aerosols. However, because the spectral reflectivity effects of a layer are dominated by the upper few optical depths these relations should not be used for conversion of optically thick layers.

Fig. 36.— A: Best fit cloud pressure boundaries retrieved from the location-3 2016 spectrum as a function of the assumed ratio of top to bottom pressures (solid curves) compared to approximations (red dashed curves) based on the assumption that the mean cloud pressure is fixed to the sheet cloud value (dashed curve). In this case the particle scale height is equal to the pressure scale height. B: Best fit pressure boundaries as a function of particle to gas scale height ratio (solid curves) for diffuse particle layers with a top pressure boundary that is just 30% of the bottom pressure, compared to approximations (red dashed curves) for those boundaries based on assuming that the mean pressure of the cloud remains fixed at all scale height ratios. Layer 2 is plotted in green at the right to help follow the boundaries that overlap with those of layer 3. The bottom panels display the χ² values for each fit.
of latitude and time. While it is a good match to our 2013 results, it strongly disagrees with our 2016 value of 0.2 \( \mu m \). Their inferred stratospheric optical depth in the \( 80^\circ \)–\( 88^\circ \)N latitude region is \( \sim 0.35 \times \) the extinction efficiency \( Q_{\text{ext}}(\lambda) \). That evaluates to \( \sim 0.008 \) at 1 \( \mu m \) (4 years after solstice), which is about 1/5 of our 2013 value (4 years before solstice) and about 1/20 of our 2016 value (1 year before solstice). Their low optical depth might be due to a rapid decline in haze optical depth after solstice, but other factors may also be at play. Perhaps most significant is that our assumed \( \text{CH}_4 \) VMR of 0.47\% (Fletcher et al. 2009b) is nearly double their assumed value of 0.25\%. Their lower value would make the stratospheric haze much more visible in the 890-nm methane band and thus would require a reduction in haze opacity above their fixed base pressure to fit the \( I/F \) seen at that wavelength. Correcting for that inappropriate reduction would bring their values closer to ours.

We do find approximate agreement in the wavelength dependence of the imaginary refractive index, at least over the 0.35 \( \mu m \) to 0.8 \( \mu m \) range. As evident in Fig. 38, their imaginary index spectral shape and absolute values for the north polar region in 1991 are in rough agreement with our results for 2013, but below the increased values we found for 2016. We also differ of course on the existence of a semi-infinite tropospheric cloud, which is more of a modeling convenience than a prediction, as Karkoschka and Tomasko (2005), do not claim sensitivity to particles deeper than \( \sim 600 \) mbar. From their north polar observations in 1991, they inferred a tropospheric particle radius of 0.15 \( \mu m \), a top pressure of 80 mbar, and a \( \tau/Q_{\text{ext}} \) value of about 2/bar, which is equivalent to an optical depth of 0.7/bar at 0.8 \( \mu m \) or 0.37/bar at 1 \( \mu m \). However, they found the best fit had no aerosols below the 400 mbar level, which translates to a mean pressure of 240 mbar for their tropospheric layer and an optical depth of 0.32 bar \* 0.37/bar = 0.12 for the total optical depth of that layer. For comparison, our putative diphosphine layer between 78\(^\circ\)N and 87\(^\circ\)N has a particle radius of 0.2 \( \mu m \), a mean pressure of 240 mbar, and an optical depth of \( \sim 0.3 \). This is relatively close agreement, except for optical depth, which might easily be due to a combination of their low \( \text{CH}_4 \) VMR choice and temporal changes.

Comparison to 2013 results. — The results of Sanz-Requena et al. (2018) are based on Cassini ISS imagery of the north polar region taken in June of 2013, and thus provide a close spatial and temporal match to the VIMS observations we used for our 2013 analysis. Their model structure (Fig. 37) has a stratospheric haze, about which they assumed a pressure range from 1 mbar to 100 mbar, a particle number density independent of height, a very low spectrally flat absorption (Fig. 38) and a fixed particle radius of 0.15 \( \mu m \). Our radius range for 2013 is 0.04–0.08
which are 70%-90% of the pressure scale height. This is quite different from our model which has a base pressure near 250 mbar, or an effective pressure of 40–60 mbar, particle radii of about 0.18 \( \mu \text{m} \) (in agreement with our 2016 radii) with 1–\( \mu \text{m} \) stratospheric optical depths about 0.025 outside the eye (about 2/3 of our 2013 mid-hexagon value and 1/7th of our 2016 values) and 0.01 inside the eye (about 1/4 of our value). For the putative \( \text{P}_2 \text{H}_4 \) layer, they found base pressures at 300–400 mbar, particle radii of 0.5–0.6 \( \mu \text{m} \), and optical depths of 0.3 inside the eye to 0.5–1 outside. Their results for this layer are in good agreement with our north polar results for 2016, except that we find lower optical depths inside the eye. The particle sizes and optical depths are both somewhat larger than our north polar results for 2013. For the ammonia layer they found base pressures near 1 bar outside the eye, decreasing to 800 mb inside the eye, particle radii of 1.5–2 \( \mu \text{m} \), decreasing to 1–1.3 \( \mu \text{m} \) inside the eye, and optical depths of about 0.6–1. Our 2016 analysis for this layer yielded somewhat lower base pressures (0.6–1 bar), somewhat larger particle radii, typically 2–3 \( \mu \text{m} \), and similar optical depths 0.2–0.9 outside the eye, but 0.1 in the eye. The biggest difference between our north polar and the 2006 south polar results is that the latter infer a stratospheric haze with larger particles and a smaller optical depth, which might be related to the difference in seasonal phase, considering that their south polar observations were obtained 4 years after solstice, while our north polar observations were obtained 4 years before solstice in 2013.

Comparison to south polar results

From a modeling similarity standpoint, the results most easily compared to our north polar results are the south polar results of [Sanz-Requena et al. (2018)], who used three compact upper layers including an \( \text{NH}_3 \) ice layer, and also used as constraints both reflected sunlight and thermal emission provided by VIMS near-IR spectra, although they did not include visual bands. Their observations are from October 2006 (4 years after southern summer solstice and thus at least 5 years in seasonal phase after our 2016 observations). For the stratospheric haze, they found an effective pressure of 0.6–1 bar, particle radii of about 0.18 \( \mu \text{m} \) (in agreement with our 2016 radii) with 1–\( \mu \text{m} \) stratospheric optical depths about 0.025 outside the eye (about 2/3 of our 2013 mid-hexagon value and 1/7th of our 2016 values) and 0.01 inside the eye (about 1/4 of our value). For the putative \( \text{P}_2 \text{H}_4 \) layer, they found base pressures at 300–400 mbar, particle radii of 0.5–0.6 \( \mu \text{m} \), and optical depths of 0.3 inside the eye to 0.5–1 outside. Their results for this layer are in good agreement with our north polar results for 2016, except that we find lower optical depths inside the eye. The particle sizes and optical depths are both somewhat larger than our north polar results for 2013. For the ammonia layer they found base pressures near 1 bar outside the eye, decreasing to 800 mb inside the eye, particle radii of 1.5–2 \( \mu \text{m} \), decreasing to 1–1.3 \( \mu \text{m} \) inside the eye, and optical depths of about 0.6–1. Our 2016 analysis for this layer yielded somewhat lower base pressures (0.6–1 bar), somewhat larger particle radii, typically 2–3 \( \mu \text{m} \), and similar optical depths 0.2–0.9 outside the eye, but 0.1 in the eye. The biggest difference between our north polar and the 2006 south polar results is that the latter infer a stratospheric haze with larger particles and a smaller optical depth, which might be related to the difference in seasonal phase, considering that their south polar observations were obtained 4 years after solstice, while our north polar observations were obtained 4 years before solstice in 2013.

### Results

The bottom aerosol layer of **Sanz-Requena et al. (2018)** is constrained by the assumption of fixed top and bottom boundaries of 1.0 bar and 1.4 bars with a fixed refractive index the same as assumed for the stratosphere, and a fixed particle radius of 10 \( \mu \text{m} \). The only fitted parameter in this case is the optical depth, which they found to be between 10 and 16, with uncertainties of 2 and 9 optical depths respectively. We did not find an aerosol layer in this pressure range. And our closest layer is between their second and third layer, with particle radii of 2–3 \( \mu \text{m} \), and an optical depth of only 0.11–0.17. Apparently our having many more spectral constraints over a wide range of wavelengths (including thermal emission) and a model with layers of distinct compositions and fitted particle sizes and pressures instead of assumed values, can lead to very different vertical distributions, particle sizes, and optical depths.
and one year before in 2016. If north-south symmetry applies to the stratospheric haze behavior, these results suggest that its optical depth increases as solstice is approached, reaches a maximum near solstice, and declines after solstice, but particle size, while increasing during the approach to solstice, is slower to decline afterwards. On the other hand, the south polar results may have found somewhat larger particles because they did not use the VIMS visual spectral constraints, or north-south symmetry may not be valid (a plausible possibility, given the absence of a south polar hexagon).

**Comparison closest in seasonal phase.** — Prior studies of the south polar region that provide the best seasonal phase match to our north polar results are those of Pérez-Hoyos et al. (2005) for 2003.7, Karkoschka and Tomasko (2005) for 2004.3, and Sánchez-Lavega et al. (2006) for 2004.3 and 2004.5, all less than 2 years past the southern summer solstice (October 2002) as shown Fig. 1 and thus less than three years apart in seasonal phase from our north polar 2016 observations. Turning first to Karkoschka and Tomasko (2005) results, we find the same disagreement on stratospheric particle size as for the north pole because they assumed the same radius of 0.08 μm for all latitudes and years. Their optical depth for the 80°S–90°S in March 2004 is \(\sim 0.5 \times Q_{\text{ext}}\), which converts to 0.012 at 1 μm. That is about 1/4 of our 2013 mid-hexagon value and less than 1/10th of our 2016 mid-hexagon value, suggesting that the post solstice decline in haze optical depth is even more rapid than suggested by the comparison with Sromovsky et al. (2020a). However, as discussed for the north polar comparison, differences in the style of vertical structure models and nearly a factor two difference in assumed methane mixing ratios adds uncertainty to the meaning of these differences.

The comparison with Pérez-Hoyos et al. (2005) is also clouded by their assumption of a low CH₄ VMR of 0.28%. Their model contained three layers as illustrated in Fig. 57. They confined their stratospheric haze to lie between 1 mbar and 10 mbar, which, combined with their low CH₄ VMR, we would expect to lead to artificially low optical depths. However, their 80°S value at 889-nm is equivalent to 0.02 to 0.04 at 1 μm, which is not far above our 2013 mid-hexagon north polar results and close to the 80°S results of Sromovsky et al. (2020a), even though closer to solstice, and thus suggesting an intermediate rate of decline. The inferred stratospheric absorption results of Pérez-Hoyos et al. (2005) are very different from our results and from those of Karkoschka and Tomasko (2005), displaying a very steep gradient from 260 nm to 450 nm, but flat at longer wavelengths (see Fig. 38).

It appears that much of the shortwave absorption that is missing from their stratospheric haze is provided by their upper tropospheric layer (see panel C of Fig. 38), which is modeled using a wavelength-dependent single-scattering albedo and phase function, but a wavelength-independent optical depth. Their upper tropospheric layer in the polar region extends from 90 mbar to 400 mbar, with about 3 optical depths for the entire layer. Our optical thickness of this layer for the mid-hexagon region of the north pole is about 0.3 optical depths in 2013 and but close to 1 optical depth in 2016, both at 1 μm. Sromovsky et al. (2020a) found particles in the 0.5 μm to 0.6 μm range for this layer in the south polar region, at an effective pressure near 300 mbar, which is somewhat deeper than the 245 mbar mean pressure of Pérez-Hoyos et al. (2005), but with an optical depth of 0.6 to 0.8 outside the eye region, which is within the lower limit of the optical depth range inferred by Pérez-Hoyos et al. (2005).

Sánchez-Lavega et al. (2006) used a model structure similar to that of Pérez-Hoyos et al. (2005) with the main exceptions being the use of spherical particles for the upper tropospheric layer and the increased stratospheric absorption they inferred in the stratosphere between 350 nm and 650 nm (see Fig. 38). Although their assumed value for the CH₄ VMR was not given, their paper predates by three years the Fletcher et al. (2009b) paper that established the current accepted value, and thus probably used the same value as Pérez-Hoyos et al. (2005). They constrained a stratospheric haze extending from 1 mbar to a fitted bottom of 30 mbar, with best fit particle radii of 0.15–0.2 μm, and an optical depth of ~0.05, which is about double that of Sromovsky et al. (2020a) and comparable to our 2013 mid-hexagon results but about 1/4 of our 2016 mid-hexagon values. They placed their tropospheric haze layer between 70–80 mbar and 150–300 mbar, with mean pressures from 110 mbar to 190 mbar, substantially lower in pressure than most other results. They inferred particle radii of 0.75–1.0 μm (comparable to Sromovsky et al. (2020a) values outside the eye), and optical depths of 0.9–1.2 μm, which are just slightly above the Sromovsky et al. (2020a) values outside the eye, but both are above the levels we found in the north polar region. The model of Sánchez-Lavega et al. (2006) also contains a putative ammonia ice cloud that is taken to be dense and semi-infinite, with a top at 500±100 mb at 80°S and 300±100 mbar at 87°S and 89.5°S. This strongly conflicts with the Sromovsky et al. (2020a) results, which put the effective pressure closer to one bar and the optical depth near 1 as well. A dense semi-infinite cloud of ammonia ice is ruled out by the thermal emission constraints near 5-μm.

Unfortunately, many of the differences we find among various results cannot be confidently interpreted as temporal (or seasonal phase) variations because of different styles of modeling, different assumptions about the methane mixing ratio and pressure boundaries, and different observational constraints, some covering just the CCD spectral range with a few bandpass filters, and others covering a wide spectral range with complete spectra. Clearly the deeper aerosol layers benefit from near-IR observations and the combined use of reflected sunlight and thermal emission.
7. SUMMARY AND CONCLUSIONS

Using the latest VIMS calibrations, we combined co-located visual and infrared VIMS spectral imaging observations of Saturn’s north polar region from just outside the hexagon region to inside the eye to create spectra spanning the range from 0.35 μm to 5.12 μm, acquired in daylight so that reflected sunlight and Saturn’s thermal emission could both be used to constrain Saturn’s vertical aerosol structure and composition. We used a model containing four compact layers of spherical particles with different compositions in each layer to create synthetic spectra for comparison with the observed VIMS spectra. Models were constrained by the observations using a Levenberg-Marquardt non-linear fitting code. The models fit the spectra well and most model parameters were well constrained by the spectra. The main results of our analysis, as constrained by our assumed model structure as well as the observations, are described in the following.

1. Layer 1, at an effective pressure generally in the 30 mbar to 50 mbar range contains sub-micron particles with significant short-wavelength absorption that plays a major role in defining Saturn’s color (this is the layer we assumed to be Saturn’s chromophore). From the hexagon boundary at about 75°N to the eye boundary at 88.8°N the layer changed significantly between 2013 and 2016: its particle sizes increased from below 0.1 μm to 0.2 μm, its optical depth increased by about a factor of 5, its column mass density decreased by about a factor of two, and its imaginary index increased by a factor of three. In the eye (from 88.8°N to the pole) there was little change in any of the parameters. The optical properties of the chromophore did not vary much with latitude over this period. While a chromophore might be present in other layers as well, the best defined and simplest fits were obtained by placing the chromophore entirely in the stratosphere.

2. Layer 2, with base pressures found generally between 250 mbar and 300 mbar, lacks near-IR absorption features that might identify its composition. We cannot rule out the photochemically preferred P$_2$H$_4$ as its main component because we do not know enough about the imaginary index of P$_2$H$_4$. Assuming the real index of P$_2$H$_4$ for this layer (1.74) leads to somewhat more consistent fits than assuming an index of 1.4. This layer has a column mass density that, if composed of P$_2$H$_4$, could be replenished by an upwelling of PH$_3$ gas that was more than 150 times smaller than sedimentation speed of particles. Between 2013 and 2016 this layer did not change much in base pressure, but between the hexagon outer boundary and the eye its optical depth increased by a factor of 3–5, and its column mass density by a similar amount, with little change inside the eye.

3. Layer 3 has a base pressure located between 950 mbar and 1.05 bars, in a pressure range where ammonia ice condensation is expected, and displays the 3-μm absorption expected of ammonia ice, which is visible when upper layers are optically thin or when the layer 3 optical depth is unusually high. A small NH$_3$ VMR of only 10 ppm in the condensation pressure to 4 bar region is sufficient to resupply the particle mass with an upwelling of gas only 1/25th of the sedimentation speed. Between 2013 and 2016 this layer also increased its optical depth and column mass density by factors of 2–3, with little change in particle radius. Generally much smaller changes were seen in the eye.

4. Layer 4, residing between 2.9 and 4.5 bars, mainly constrained by its effect on thermal emission, is plausibly partly composed in part of a mix of NH$_4$SH and water ice but seems to need additional absorption to better match the thermal emission spectrum near 5 μm and to limit scattering contributions at short wavelengths. Our empirical model provide better fits than either NH$_4$SH or H$_2$O. Our retrievals find very large particles, with radii of 10’s of μm. Its column mass density far exceeds all other layers, and outside the eye seems to have increased by roughly a factor of three between 2013 and 2016. This layer also exhibits essentially no time dependence inside the eye.

5. An accurate measure of the color of the polar region, using full spectra instead of bandpass filter samples, shows that the color change within the hexagon region was from blue/green to gold and could be entirely explained by changes in a stratospheric chromophore layer: a doubling of its optical depth, a doubling of its particle radius, and a tripling of its imaginary index. The large spectral changes in the near-IR region are mainly due to a factor of 3–10 increase in the optical depth of the putative diphosphine layer (Layer 2 of our model).

6. VIMS observations are not sensitive to the deep value of the NH$_3$ VMR, but somewhat sensitive to its VMR in the depleted region between about 4 bars and the NH$_3$ condensation level at generally less than 1 bar in our results. In 2013, aerosol optical depths were low enough that within the hexagon, including the eye region, we were able to retrieve reasonably well constrained values of about 50 ppm. But where aerosol optical depths were much greater, as at all latitudes in 2016 (except in the eye), and just outside the hexagon boundary in both years, the retrieved best-fit VMR values were very low and very uncertain, with upper limits of the uncertainty range approaching 2013 values in some cases.

7. We found average arsine VMR values of 2.18±0.19 ppb in 2013 and 1.76±0.08 in 2016,
with standard deviations of 0.54 ppb and 0.24 ppb respectively. The slightly higher values in 2013 are due mainly to higher values inside the hexagon, where aerosol opacity was generally low at that time, suggesting that arsine declines with altitude above the cloud level.

8. With an assumed small fractional scale height above an adjustable breakpoint pressure, below which a deep mixing ratio was derived, we found a virtually constant deep PH₃ VMR of 5 ppm, and a variable breakpoint pressure almost always near the top of the main aerosol layer (Layer 2). But where that layer had very small optical depth, the best-fit pressure breakpoint moved just to beyond the next deeper layer (ammonia ice cloud), suggesting that the cloud layers provide protection against UV photolysis that efficiently destroys PH₃ above them, as suggested in previous publications.

9. While our compact layers were assumed have top pressures that were 90% of their bottom pressures, we found that high quality fits could also be obtained with thicker layers, and provided equations to transform layer parameters to values appropriate to thicker layers. In one case we found that setting top pressures of all layers to 60% of their bottom pressures resulted in somewhat improved fit quality. Another case found thinner layers were preferred. This is an area that merits further investigation.

10. Location 2 from 2013 happened to sample a ring of clouds at 88.5°N that displayed unusual spectral features that are associated with enhanced optical depths in the ammonia ice layer. Retrievals confirming this also found unusually low PH₃ breakpoint pressures, and enhanced deep PH₃ VMR values, suggesting local upwelling motions. The enhanced optical depth of layer 3 allowed us to confirm its identity by comparing fit quality assuming the NH₃ refractive index with the qualities obtained assuming NH₄SH (χ² increased by 50), and a simple real index of 1.4 (χ² increased by almost 90), providing strong evidence in favor of our chosen composition. Applying the same test to a bright discrete feature from 2013 location 11, the χ² increases were by huge values of 690 and 1070 respectively, providing overwhelming preference for NH₃ ice as the composition of layer 3 particles.

11. Comparisons with prior published models of southern and northern polar regions are roughly consistent with the idea that stratospheric hazes in both polar regions rise in optical depth as their summer solstice approaches and decline following solstice, but differences in model styles, constraints, and assumed values of the CH₃ VMR, as well as differences in chromophore models, add considerable uncertainty to the comparisons with prior models. All of these results must be understood within the context of our assumed model structure. There are likely other models that could be constructed to fit the spectra just as well. It should also be remembered that we have not thoroughly explored the enormous 18-20 dimensional space of parameter variation, so that there might also be other solutions even within the constraints of our assumed model structure. Further improvements might be made by using a variety of methods to effectively improve the signal to noise ratios of the observations by spatial averaging or simultaneously fitting observations at different view angles within a given latitude band. It would also be valuable to have laboratory measurements of the optical properties of diphosphine from UV to the thermal infrared.

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