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ABSTRACT

Saturn was observed in the vicinity of the $J = 10$ manifold of the pure rotational band of phosphine on 1984 July 10 and 12 from NASA's Kuiper Airborne Observatory with the facility far-infrared cooled grating spectrometer. On each night observations of the full disk plus rings were made at 4 to 6 discrete wavelengths which selectively sampled the manifold and the adjacent continuum. The previously reported detection of this manifold is confirmed. After subtraction of the flux due to the rings, the data are compared with disk-averaged models of Saturn. It is found that PH$_3$ must be strongly depleted above the thermal inversion (~70 mbar). The best fitting models consistent with other observational constraints indicate that PH$_3$ is significantly depleted at even deeper atmospheric levels (~500 mbar), implying an eddy diffusion coefficient for Saturn of $-10^4$ cm$^2$ sec$^{-1}$. 
I. INTRODUCTION

The presence of phosphine (PH$_3$) in Saturn's troposphere has been well established by observations at near and middle infrared wavelengths (Larson et al., 1980 and references therein; Hanel et al., 1981). This was somewhat surprising because thermochemical equilibrium calculations indicated that for temperatures \( \leq 2000 \) K phosphine would react with H$_2$O (Lewis, 1969; Barshay and Lewis, 1978). However, its presence may be explainable by some combination of modest convection, an upper atmospheric recycling mechanism, and low abundances of H$_2$O and NH$_3$ (Larson et al., 1980). The observed PH$_3$ abundance implies that the P/H ratio is approximately 3 times the solar value (Encrenaz and Combes, 1980 and references therein; Courtin et al., 1984), which may have interesting implications for cosmogony (Gautier and Owen, 1983).

Moreover, the vertical distribution of PH$_3$ is important to our understanding of its chemistry and the vertical dynamics on Saturn (Prinn and Lewis, 1975; Strobel, 1978; Larson et al., 1980). From IUE ultraviolet spectra Winkelstein et al. (1983) concluded that there is little or no PH$_3$ above 25 mbar, but from Voyager IRIS spectra Courtin et al. (1984) inferred a uniform mixing ratio of \( 3.0 \pm 0.5 \times 10^{-6} \) (5X solar) up to the 3-5 mbar level. Given the PH$_3$ abundance inferred at shorter wavelengths, the far infrared manifolds of the pure rotational band of PH$_3$ are predicted to be quite strong (Encrenaz and Combes, 1977). This band is expected to reach optical depth unity near the thermal inversion (-70 mbar), thereby probing higher levels of the atmosphere than the near and middle infrared vibrational transitions (Encrenaz and Combes, 1980). Observations of this
band will therefore place new constraints on the PH, distribution in the vicinity of the tropopause.

Haas et al. (1984) previously detected the $J = 10$ manifold at 103 $\mu$m and Viscuso (1984)\textsuperscript{1} may have detected the $J = 7$ manifold at 141 $\mu$m. In this paper we report new observations of the $J = 10$ manifold with higher signal-to-noise and improved calibration. We also describe our ring subtraction procedure and present a number of disk-averaged theoretical models. The implications of the best fitting models are discussed.

II. OBSERVATIONS AND DATA ANALYSIS

Saturn was observed on the nights of 1984 July 10 and 12 with the facility far-infrared cooled grating spectrometer (CGS) on the 91 cm telescope of the Kuiper Airborne Observatory from an altitude of 12.0 km. The FWHM beam size was 40" and the chopper throw was $\sim$4'. The CGS was operated with six discrete Ge:Ga detectors in the dispersed focal plane with a wavelength separation of 0.0314 $\mu$m at 103 $\mu$m. The detectors oversampled the spectrum in wavelength by a factor of about 1.8. Additional details regarding the CGS design, performance, and typical observing procedures are described in Erickson et al. (1984a,b; 1985).

The resolution of the CGS is high enough that an entire PH, manifold ($\sim$3 $\mu$m wide) could not be scanned in the available observing time ($\sim$15 min). Hence observations were made at 4 to 6 discrete wavelengths (grating positions) which were chosen to minimize the effects of telluric absorption (see Figure 1a) and optimize the wavelength coverage of the important spectral features. Four pairs of right-left beam integrations totaling 80

\textsuperscript{1}Private communication
sec were taken at each wavelength. The absolute flux calibration and the relative detector response were obtained by observing Mars on the same flights. The final spectra are simply the ratio of the signals measured on Saturn to those measured on Mars and multiplied by the Mars flux corresponding to a brightness temperature of 227 K at all wavelengths as predicted by the model of Simpson et al. (1981). At this epoch the diameter of the Martian disk was 13.18", the Saturnian disk was 17.39" x 15.71", and the inclination of the rings was 18.99° (Vohden and Boksenberg, 1984). Following Matthews and Erickson (1977), we calculated the total area of the Saturn ring-disk system to be 405.0 square arcsec. The Saturn flux was increased by 6% to account for the effects of diffraction in the telescope and geometrical losses due to the extended nature of the rings relative to the beam. No second order water vapor correction was applied because the two planets were observed at a similar elevation and aircraft heading and there are no strong telluric features at the wavelengths in question (Figure 1a).

The brightness temperatures measured for the Saturnian ring-disk system are plotted in Figure 1b and listed in Table 1. A decrease in brightness temperature of ~5 K at the expected position of the J = 10 manifold of PH₃ is clearly evident in both data sets. No other molecules are expected to produce absorption or emission features at these wavelengths; the J = 4 manifold of NH₃ (cf Figure 2) has been carefully avoided. To improve the signal-to-noise, the six detectors have been averaged at each grating position. Their total bandpass is 0.19 μm and the uncertainty in the wavelength is ~0.015 μm. The quoted error bars are statistical errors only; they represent one-standard-deviation-of-the-mean for the six detectors.
Systematic uncertainties will increase these errors somewhat, but are
difficult to estimate. There is a 15% difference in the absolute
calibration between the two nights' data. However, the good night-to-night
agreement in the shape of the overall spectrum suggests that the relative
calibration of the data points on a single night is significantly better.

III. THE RING SUBTRACTION PROCEDURE

The contrast in the PH$_3$ line is reduced by the continuum emission of
the rings. In order to directly compare our measurements with models of the
disk of Saturn, we must subtract the ring contribution. To this end, we
have constructed a model of the ring-disk system for the appropriate epoch.
Following Haas et al. (1982; henceforth HEMGC), the total flux from the
Saturn system is

$$\Omega B_\nu (T) = [\Omega_{VD} + \sum \omega_i \csc^{-\tau_i} |B|] B_\nu (T_D) + \sum \omega_i B_\nu (T_R),$$  \hspace{1cm} (1)

where $B_\nu$ is the Planck function, $\Omega_t$ is the total solid angle of the
ring-disk system, $\Omega_{VD}$ is the solid angle of the visible disk, and $|B|$ is the
ring tilt angle with respect to the Earth. The average brightness
temperatures $T$, $T_D$, and $T_R$ are those of the system, the disk, and the rings,
respectively. The i-th ring surface has a normal optical depth $\tau_i$, a
visible solid angle $\omega_i$, and a visible solid angle overlapping the disk $\omega_i$.

The rings are divided into five separate surfaces as described in HEMGC.
The optical depths $\tau_i$ vary as $\sqrt{\omega}$. $T_R$ is computed from a
thermometric temperature $T_o$ and an emissivity dependent on the $\tau_i$'s (see
HEMGC equation 5 and Figure 6). A fit to the data of HEMGC gives $\alpha = 1.5$
and \( T_\circ = 88.7 \text{ K} \) for \(|B| = 21.4^\circ\). If the 100 \( \mu \text{m} \) brightness temperature variation with \(|B|\) has the same form as at 20 \( \mu \text{m} \) (Nolt et al., 1980), then \( T_\circ \) should be decreased by \( \leq 2 \text{ K} \). This effect has been ignored since it results in a negligible change in the depth of the \( \text{PH}_3 \) line.

This model for the rings was combined with our standard disk model (section IV) using equation (1). Since we are primarily concerned with the shape of the spectrum and not with its absolute calibration, we then renormalized the two nights' data to this model. This renormalization removes the difference in absolute calibration between the two data sets, forces the relative contributions of the disk and rings to be the same as in HEMGC (allowing for the changes in geometry with \(|B|\)), and ensures that the disk spectrum obtained by subtracting the ring contribution from our data will have the same normalization as our standard disk model. The renormalization factor is 0.84 for July 10 and 0.98 for July 12.

The ring contribution was then subtracted from the measured (renormalized) spectrum using equation (1) and the ring model described above for \( T_R \). The inferred disk spectrum for each night is shown in Figure 2 (circles) along with our standard disk model. The error bars again reflect statistical errors only. The measured contrast in the line is just over half that of the model. Increasing the contribution of the rings to the total system flux will increase the contrast in the deduced disk spectrum. For example, if we repeat the subtraction process assuming the optical depth of the rings is independent of frequency (\( \alpha = 0 \)), then \( T_R \) at 100 \( \mu \text{m} \) increases from 63 K to 77 K (cf HEMGC's Figure 6) and the contrast in the line is increased by several kelvins (Figure 2; triangles). However,
there is strong evidence that the brightness temperature of the rings turns over beyond 50 μm (HEMGC; Daniel et al., 1982; Melnick et al., 1983). Therefore, the discrepancy between the measured line profile and our standard disk model is probably not a result of uncertainties in the ring subtraction procedure. In the following sections we only consider the disk spectrum derived assuming that $T_R$ decreases as in HEMGC (our case $\alpha = 1.5$).

IV. SATURN DISK MODELS

Disk-averaged models of Saturn were generated using the computer code described in HEMGC and Goorvitch et al. (1979). The PH$_3$ mixing ratio was parameterized as $x = x_0(P/P_o)^\beta$ for $P < P_o$ and as $x = x_0$ for $P \geq P_o$, where $P$ is the total pressure and $\beta$ is the ratio of the dynamical scale height ($h_p = RT/\mu g$) to the scale height for decreasing the PH$_3$ mixing ratio $h_x$ (cf Encrenaz and Combes, 1977; Strobel, 1978; Tokunaga et al., 1980). Our standard model uses $P_o = 100$ mbar, a PH$_3$ scale height $h_x = 5$ km, $x_0 = 1.2E-06 = 2x_0$ (twice solar), a helium-to-hydrogen mixing ratio of 0.13/0.87, an ammonia mixing ratio of 1.5×10$^{-4}$, and the pressure-temperature profile of Tokunaga and Cess (1977), which is very similar to that obtained by Voyager (Hanel et al., 1983).

The wavelengths for the pure rotational band of PH$_3$ were calculated from the formula and constants given by Maki et al., (1973). Because of the lack of experimental data, the strengths were calculated using the formulas for NH$_3$, which is a spectroscopically similar molecule. We assumed a permanent dipole moment of 0.574 Debye (Poynter and Pickett, 1980), adopted the pressure broadening data of Pickett et al. (1981), and used a Lorentzian
line profile (cf Encrenaz et al., 1971). A ±10% variation in the \( \text{PH}_3 \) line strengths results in a brightness temperature change of less than ±0.3 K.

As shown in Figure 2, our standard model shows considerably more contrast in the \( \text{PH}_3 \) line than is observed. We have investigated the dependence of this contrast on the parameters of the \( \text{PH}_3 \) distribution \((x_o, P_o, \text{and} h_x)\), the \([\text{He}]/[\text{H}]\) mixing ratio, and the pressure-temperature profile. The models are relatively insensitive to the helium-to-hydrogen mixing ratio. Varying \([\text{He}]/[\text{H}]\) from 0.20/0.80 to 0.06/0.94 changes the brightness temperature in the continuum by ≤0.4 K. Since the core of the line is formed near the inversion (~70 mbar), an inversion temperature of ~93 K is required to reduce the model contrast to that which is observed. Such variations in the pressure-temperature profile are inconsistent with past observations, including the Voyager IRIS experiment (Hanel et al., 1983) and the radio occultation mean (Tyler et al., 1982).

The brightness temperature in the core of the line roughly corresponds to the atmospheric level where the optical depth reaches unity. For a given pressure-temperature profile, the most straightforward way to raise the brightness temperature in the core is to either increase or decrease the opacity such that \( \tau = 1 \) lies above or below the thermal inversion. Figure 3 shows the effect of decreasing \( P_o \), the pressure above which the \( \text{PH}_3 \) mixing ratio falls exponentially, from 100 to 10 mbar. Such models place significant amounts of \( \text{PH}_3 \) in the stratosphere, producing a strong emission line core. Note that the data points at 102.41 and 102.92 \( \mu \text{m} \) lie near the minimum brightness temperature in the manifold, whereas the data point at 102.78 \( \mu \text{m} \) lies near the maximum of the emission core. These models are
inconsistent with the observations, which show a similar brightness temperature at all three wavelengths. The strength of the emission core is reduced somewhat if we use the pressure-temperature profile deduced from Voyager 2 radio occultation measurements (Tyler et al., 1982), because it has significantly cooler temperatures above the inversion (cf Orton, 1983). However, such models still produce a substantial emission core which is inconsistent with the present observations.

Varying the scale height $h_x$ gives results similar to those in Figure 3. That is, increasing $h_x$ to 10 km puts more PH$_3$ above the tropopause and produces an emission line core similar to the model with $P_o = 50$ mbar. From the present observations we therefore conclude that PH$_3$ must be strongly depleted above the inversion. Tokunaga et al. (1980) and Winkelstein et al. (1983) arrive at similar conclusions based on observations in the near infrared and the ultraviolet, respectively. However, Courtin et al. (1984) find evidence in the Voyager IRIS spectra at 10 μm for a uniform mixing ratio of 5X solar to an altitude of 3 to 5 mbar. Prinn et al. (1984) suggest that this discrepancy may result from the nonuniqueness of the thermal inversion process or to latitudinal or seasonal changes in the PH$_3$ vertical profile. Theoretical models predict that phosphine should be strongly depleted in the stratosphere because of photolysis by ultraviolet radiation (Prinn and Lewis, 1975; Strobel, 1977; 1978). Similar depletions have been observed on Jupiter (e.g., Tokunaga et al., 1979; Kunde et al., 1982).

An acceptable fit to the present observations can be obtained if a stratospheric "cloud" or haze is included in our standard model with an
optical depth of 0.25 at 100 μm. In such a model the PH₃ manifold is still formed above the inversion, but without a significant emission core. However, it may be difficult to make particles large enough to absorb at 100 μm and still small enough to remain buoyant at pressures ≤100 mbar (Orton, 1983). Moreover, there is little independent evidence for the existence of large stratospheric particles in other spectral bands (Tomasko et al., 1984).

As discussed above, the brightness temperature in the PH₃ manifold can also be raised by forming the line below the inversion. In Figure 4 we show the results of varying x₀, the uniform mixing ratio assumed for P > P₀. The manifold becomes increasingly narrow as the mixing ratio is decreased. However, the brightness temperature in the core remains nearly constant until the mixing ratio is sufficiently small (x₀ ≤ 0.05x₀) to permit formation of the core (τ - 1) below the inversion at higher temperatures. Such models are able to fit the observed core of the manifold, but require x₀ << x₀, which is inconsistent with the near and middle infrared observations which find x₀ - 2 - 5x₀ in the lower troposphere (Tokunaga et al., 1980; Larson et al., 1980; Courtin et al., 1984).

Since the near and middle infrared vibrational transitions probe deeper into the troposphere (cf. Encrenaz and Combes, 1980), a consistent model can be obtained by keeping x₀ ≥ 2x₀ and increasing P₀. Such models maintain a large abundance of PH₃ in the lower troposphere, but show substantial depletions in the vicinity of the tropopause. Figure 5 shows the effect of increasing P₀ from 100 mbar to 1 bar. The model with P₀ = 500 mbar provides an excellent fit to our measured profile.
Moreover, the inferred phosphine distribution is remarkably similar to that preferred by Kaye and Strobel (1984), who consider the detailed photochemistry of Saturn's atmosphere and derive PH₃ distributions for different values of the eddy diffusion coefficient (K). Our best fitting distribution (P₀ = 500 mbar, hₓ = 5 km, and x₀ = 2Xₒ) closely corresponds to the one they calculate for K = 10⁴ cm² sec⁻¹ in the upper troposphere. Similar values of K are inferred from observations of ortho and para hydrogen on the Jovian planets (Massie and Hunten, 1982).

V. CONCLUSIONS

The main conclusions of this paper are:

(1) The detection of the far-infrared J = 10 pure rotational manifold of phosphine (PH₃) on Saturn has been confirmed,

(2) The lack of a significant emission core in this manifold implies that there is little or no PH₃ above the inversion, and

(3) The most straightforward explanation for the relatively low brightness temperature contrast in the J = 10 manifold is a significant depletion of PH₃ in the upper troposphere (P₀ ≤ 500 mbar). This suggests that the eddy diffusion coefficient in Saturn's troposphere is ~10⁴ cm² sec⁻¹.

Improved sampling of the individual manifolds, as well as observations of several additional manifolds, would be useful in further elucidating the details of the PH₃ distribution in the vicinity of the tropopause.
ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure 1. (a) The atmospheric transmission at 12.5 km for 10 precipitable microns of water (typical) at a resolution of $\lambda/\Delta\lambda = 5000$. (b) The measured brightness temperatures of the ring-disk system of Saturn (circles are for July 10; triangles are for July 12). The error bars represent statistical errors only.

Figure 2. The circles represent the data of Figure 1 with the contribution of the rings removed assuming their optical depth falls off as $v^{1.5}$ (cf. HEMGC). The triangles are the same data with the contribution of the rings removed assuming their optical depth is independent of frequency ($\alpha = 0$). The solid curve shows our standard disk-averaged model of Saturn at the same resolution.

Figure 3. The data are from Figure 2 (circles are July 10; triangles are July 12) with the ring component removed assuming $\alpha = 1.5$. The curves are disk models with different values of $P_o$, the pressure level below which the PH₃ mixing ratio is constant rather than exponential. As $P_o$ decreases, the amount of stratospheric PH₃ increases. The model with $P_o = 100$ mbar is the standard model described in the text. Recall that the data have been normalized to force the two continuum points to fit this model.

Figure 4. The data are the same as in Figure 3. The models have different values of $x_o$, the (uniform) mixing ratio for $P \leq P_o = 100$ mbar, ranging from 0.04 to 4 times solar.

Figure 5. The data are the same as in Figure 3. The models have different values of $P_o$, all at or below the tropopause.
Fig. 1a, 1b

10 μm H2O

ATMOSPHERIC TRANSMISSION, percent

SATURN (DISK + RINGS)

BRIGHTNESS TEMPERATURE, K

WAVELENGTH, μm

JULY 10
JULY 12
Fig. 5
Saturn was observed in the vicinity of the J = 10 manifold of the pure rotational band of phosphine on 1984 July 10 and 12 from NASA's Kuiper Airborne Observatory with the facility far-infrared cooled grating spectrometer. On each night observations of the full disk plus rings were made at 4 to 6 discrete wavelengths which selectively sampled the manifold and the adjacent continuum. The previously reported detection of this manifold is confirmed. After subtraction of the flux due to the rings, the data are compared with disk-averaged models of Saturn. It is found that PH₃ must be strongly depleted above the thermal inversion (~70 mbar). The best fitting models consistent with other observational constraints indicate that PH₃ is significantly depleted at even deeper atmospheric levels (~500 mbar), implying an eddy diffusion coefficient for Saturn of ~10⁴ cm² sec⁻¹.
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