Upper limits for PH$_3$ and H$_2$S in Titan’s atmosphere from Cassini CIRS

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Abstract

We have searched for the presence of simple P and S-bearing molecules in Titan’s atmosphere, by looking for the characteristic signatures of phosphine and hydrogen sulfide in infrared spectra obtained by Cassini CIRS. As a result we have placed the first upper limits on the stratospheric abundances, which are 1 ppb (PH$_3$) and 330 ppb (H$_2$S), at the 2-σ significance level.

Keywords: Titan, Titan, atmosphere, Abundances, atmospheres, Atmospheres, Composition, Saturn, satellites

1. Introduction

To date, no molecules bearing the light elements phosphorus (P) and sulfur (S) have been detected in the atmosphere of Titan by either remote sensing or in-situ methods. However, from cosmological considerations both P and S must have been present in the icy planetesimals that formed Titan,
and also delivered in trace quantities by later impacts. P in the form of PH$_3$ is found in Jupiter’s atmosphere at approximately solar abundance, while on Saturn its abundance is around 3$\times$ solar (Owen and Encrenaz, 2003). This enrichment is in line with core-accretion models, which predict that Saturn had a larger ice-to-gas fraction in its formation compared to Jupiter. Sulfur is enriched on Jupiter by 2.5$\times$ solar (Niemann et al., 1998) (and not yet detected on Saturn), perhaps due to easy formation of H$_2$S clathrate hydrates (Owen and Encrenaz, 2003). Both P and S should therefore be present in Titan’s bulk composition at fractions greater than those on Saturn, since the ice to gas ratio must have been much higher.

Fortes et al. (2007) considered a possible role for sulfur compounds in Titan cryovolcanism, suggesting that ammonium sulfate could form a magma in Titan’s mantle. Plumes of this magma could dissolve methane present in crustal clathrates, allowing explosive release to the surface. One prediction of this model is that ammonium or other sulfates should be detectable spectroscopically on Titan’s surface, as is the case on Europa and Ganymede. Such a model would presumably also release trace amounts of sulfur into Titan’s atmosphere, especially in the wake of eruptions. Pasek et al. (2011) focused on the role of phosphorus in Titan, arguing that it could be delivered both endogenously and exogenously to the surface. Phosphine is efficiently trapped in clathrate hydrates, and Pasek et al. (2011) show that all clathrates that trap H$_2$S also trap at least as much PH$_3$. Moreover, they show that PH$_3$ is more soluble in organic liquids than in water, and therefore any phosphine released from melted clathrates could be dissolved in Titan’s hydrocarbon lakes, and would participate in the hydrocarbon meteorological cycle.
We have therefore searched the infrared spectrum of Titan for the signatures of the two most likely carriers of P and S: phosphine (PH$_3$) and hydrogen sulfide (H$_2$S). Our data is from the Composite Infrared Spectrometer (CIRS, Flasar et al., 2004), carried onboard the Cassini spacecraft, which has been making close flybys of Titan since attaining Saturn orbit in mid-2004. Both gases have signatures in the 8–11 $\mu$m (1250–900 cm$^{-1}$) range, which is largely free of the hydrocarbon emissions that dominate much of Titan’s infrared spectrum. We first model and subtract out the emissions of known species including methane (CH$_4$), acetylene (C$_2$H$_2$), ethylene (C$_2$H$_4$) and deuterated methane (CH$_3$D). We then add H$_2$S and PH$_3$ incrementally to our spectral calculation using standard line lists from HITRAN (Rothman et al., 2009), and compare the predictions to the remaining Titan spectrum.

By comparing the model predictions to the instrument noise level at the 1, 2, and 3-$\sigma$ levels, we have derived the first numerical upper limits on the prevalence of H$_2$S and PH$_3$ in Titan’s stratosphere. We follow a report of our results with a discussion of the implications for existing models, and finish with some conclusions about the prospects for future searches.

2. Method

2.1. Instrument and Dataset

The Cassini CIRS instrument is a dual design, comprising mid-infrared (1400–600 cm$^{-1}$) and far-infrared (600–10 cm$^{-1}$) spectrometers, both with a FWHM (full-width to half-maximum) spectral resolution variable from 0.5–15.5 cm$^{-1}$ after Hamming apodization. The mid-IR Michelson spectrometer employs two 1 x 10 detector arrays: focal plane 3 (FP3, 600–1100 cm$^{-1}$)
and focal plane 4 (FP4, 1100–1400 cm\(^{-1}\)). Both arrays have square pixels
with fields of view 0.3 mrad across. FP4 has the highest sensitivity (lowest
background noise) and least instrumental interferences, and was consequently
used in this study.

The observations were described in an earlier paper [Nixon et al., 2010].
The spectra were acquired during the 55\(^{th}\) Titan flyby (T55) of Cassini on
May 22\(^{nd}\) 2009, in a four-hour period when the spacecraft was at a range
of 116,000–177,000 km. The observation (known as ‘MIRLMPAIR’-type)
was targeted at Titan’s limb, with the two arrays above and parallel to the
horizon. FP4 was above FP3, with the pixels centered at an altitude of 247
km (0.27 mbar) and spanning approximately 44 km (just under one scale
height) in the vertical direction at the mid-point of the observation. Using
CIRS PAIR mode, all ten detectors simultaneously recorded data, paired into
five receiver channels. A total of 941 pair-mode spectra at 0.5 cm\(^{-1}\) resolution
were selected and then averaged to create a single, high signal-to-noise (S/N)
ratio spectrum.

2.2. Spectral Modeling

The CIRS FP4 limb spectrum was then modeled to remove the signatures
of known gas species. These included CH\(_4\) (\(\nu_4\) band at 1305 cm\(^{-1}\)) and
CH\(_3\)D (\(\nu_6\) band at 1156 cm\(^{-1}\)), plus some weaker contributions from the
hydrocarbons C\(_2\)H\(_4\) and C\(_2\)H\(_2\). The modeling closely follows that described
in a recent paper [Nixon et al., 2012], and is briefly summarized here.

An initial vertical atmospheric model was created with 100 layers equally
spaced in log pressure from 1.45 bar to 0.05 \(\mu\)bar, based on the temper-
ature profile and major gas abundances (N\(_2\), CH\(_4\), H\(_2\)) determined by the
Huygens probe (Fulchignoni et al., 2005; Niemann et al., 2010). Other gas species (C₂H₄, C₂H₂) were included with constant vertical abundances in the stratosphere, at initial values taken from previous CIRS measurements at low latitudes (Coustenis et al., 2010). Similarly a uniformly mixed (constant particles/g atmosphere) stratospheric haze was included with optical properties from Khare et al. (1984). The forward radiative transfer model was computed using the NEMESIS code (Irwin et al., 2008) applied to the model atmosphere and using the HITRAN gas line atlas (Rothman et al., 2009), and then convolved with the FP4 detector spatial response shapes (Nixon et al., 2009b) to generate a model spectrum.

At this point the model was iterated to arrive at an optimum fit to the measured spectrum, by adjusting the model temperature profile (at each layer) and uniform vertical gas abundances of C₂H₂ and C₂H₄, to minimize a cost function similar to a $\chi^2$ figure of merit. This approach has been successfully used to fit the T55 limb spectrum of Titan in previous work (Nixon et al., 2009a, 2010). Fig. 1 (a) shows the best fit to the data. Note that a weak band of propane ($\nu_7$ at 1158 cm$^{-1}$) was not included in the model, as a line list for this band has yet to be produced, and shows clearly in the data-model residual (Fig. 1 (b)). The strong CH₄ $\nu_4$ band is fitted reasonably well, but also shows some residual mismatch, which may be due to imperfect knowledge of the underlying haze (continuum) opacity and/or wavelength calibration uncertainties.

2.3. Determination of Abundance Upper Limits

To search for PH₃ and H₂S, we avoided spectral regions that showed non-random ‘noise’ residual: especially the C₃H₈ $\nu_7$ region (1140–1200 cm$^{-1}$) and
the CH\(_4\) region (\(\tilde{\nu} > 1250\) cm\(^{-1}\)). This permitted us to search for the \(\nu_4\) band of PH\(_3\) around 1120 cm\(^{-1}\), and for a portion of the weak H\(_2\)S \(\nu_2\) band at 1200–1250 cm\(^{-1}\) (see Fig. 1 (c) and (d)). The summed line strengths in these regions were \(1.40 \times 10^{-18}\) cm molecule\(^{-1}\) for 1121 lines of PH\(_3\) from 1080–1140 cm\(^{-1}\), and \(2.2 \times 10^{-20}\) cm molecule\(^{-1}\) for 130 lines of H\(_2\)S at 1200–1250 cm\(^{-1}\), using line data from HITRAN (Rothman et al., 2009). Note that the PH\(_3\) band intensity was almost 100\(\times\) that of H\(_2\)S in the spectral ranges considered, so we expect 100\(\times\) greater sensitivity to PH\(_3\) compared to H\(_2\)S.

These two gas species were added to the best-fit atmospheric model at fixed trial abundances of 1 ppb with other gases and temperature held constant at the previously retrieved values, and NEMESIS was allowed to retrieve a ‘best fit’ abundance for the new species. In both cases, these retrievals resulted in no statistically significant improvement to the model \(\chi^2\), hereafter designated \(\chi^2_0\): the minimum \(\chi^2\). We then proceeded to calculate upper limits to the abundances, following the approach of Teanby et al. (2009) and Nixon et al. (2010). Starting with very low trial gas abundances in the model, these were increased incrementally, and at each value the forward spectral model was calculated, without optimized fitting or inversion, and the data-model \(\chi^2\) computed. As the trial gas abundances increase, so too does the \(\Delta\chi^2 = \chi^2 - \chi^2_0\). See Fig. 2. Following Press et al. (1992) the 1, 2 and 3-\(\sigma\) upper limits to the gas abundances occur at \(\Delta\chi^2 = 1, 4, 9\).

3. Results and Discussion

Table 1 shows our results. The derived 1, 2, 3-\(\sigma\) maximum abundances for PH\(_3\) are 0.3, 1.1, 2.2 ppb respectively, while the corresponding values for H\(_2\)S
are 91, 330, 700 ppb. The H$_2$S upper limits are some two orders of magnitude higher than those of PH$_3$ as expected, due to the much weaker band intensity in the spectral region considered, along with a higher 1-$\sigma$ NESR (Noise Equivalent Spectral Radiance) level in the corresponding spectral interval (0.6 versus 0.3 nW cm$^{-2}$ sr$^{-1}$/cm$^{-1}$).

Sulfur compounds have been suggested to play a role in Titan cryovolcanism (Fortes et al., 2007), and therefore be present in trace amounts in Titan’s atmosphere. Phosphorus is also easily dissolved in organic solvents, and as such could be a component of Titan’s present-day methane-ethane lakes, and participate in the hydrocarbon cycle (Pasek et al., 2011). A simple calculation tracing the saturation vapor pressure (data from public NIST and CRC databases) up through Titan’s troposphere using the Huygens temperature profile, indicates that abundances of PH$_3$ and H$_2$S that could reach the stratosphere are 6 and 0.035 ppb respectively. Therefore, our 2-$\sigma$ upper limit of 1 ppb for PH$_3$ provides some constraint on tropospheric PH$_3$, while our H$_2$S limit of 330 ppb is four orders of magnitude greater than allowed in this scenario and is not constraining.

At the present time, the lack of detection of P or S-bearing species anywhere in Titan’s atmosphere has caused these elements to be omitted from present photochemical models, so we have no predictions for comparison. In future, it could be interesting for such models to allow for some injection of P and S molecules into the atmosphere through a putative eruption, and to investigate subsequent chemistry, for example, conversion of sulfates to sulfides.
4. Conclusions and Further Work

In this paper we have searched for simple compounds of phosphorus and sulfur in Titan’s infrared spectrum recorded by Cassini CIRS, placing the first upper limits on the abundance of PH$_3$ and H$_2$S. In the stratosphere at 247 km we find that no more than 1 ppb of PH$_3$ and 330 ppb of H$_2$S can be present, at the 2-σ level of significance. Some potential exists for improving on these upper limits using CIRS, e.g. by future measurements at a lower limb altitude where the atmospheric density is greater. The peak sensitivity for weak trace gases is often near 10 mbar (∼100 km), at least at low latitudes, so a repeat measurement in the lower stratosphere may yield more stringent limits.

Searching in the far-IR spectrum may prove helpful in the case of H$_2$S, which has rotational lines at 50–150 cm$^{-1}$ that are some 100× stronger than the $\nu_2$ considered here. However in this region the NESR of CIRS FP1 is more than 10× higher than that of the FP4 detectors used in this work, and suffers from systematic noise artifacts. Nevertheless, the sub-mm range has already proved productive for molecular line searches by instruments such as Herschel and ground-based sub-mm telescopes, resulting in the detections of CH$_3$CN [Marten et al. 2002] and HNC [Moreno et al. 2011], and will doubtless reveal further new species in due course.

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| Gas   | Lat. (mbar) | Band | Range (cm$^{-1}$) | NESR* | Upper Limits (ppb) |
|-------|-------------|------|-------------------|-------|--------------------|
| PH$_3$ | 25°S        | $\nu_4$ | 1080–1140 | 0.29  | 0.30 1.1 2.2      |
| H$_2$S | 25°S        | $\nu_2$ | 1200–1250 | 0.64  | 91 330 700        |

*Noise Equivalent Spectral Radiance averaged over the spectral interval, in units of nW cm$^{-2}$ sr$^{-1}$/cm$^{-1}$. 
Figure 1: (a): CIRS limb average spectrum of Titan from T55 flyby (black) and model fit (green). (b): data-model spectral residual. Note the $v_7$ band of $\text{C}_3\text{H}_8$ at 1158 cm$^{-1}$ that is not included in our model (see text for details). (c) and (d) show the density and strengths of lines of $\text{PH}_3$ and $\text{H}_2\text{S}$ respectively in the interval considered.
Figure 2: Calculation of upper limits for the abundances of H$_2$S and PH$_3$ in Titan’s stratosphere. (a) & (c): residual of fit to the CIRS Titan spectrum in each region, after the modeling and removal known gas species (black line). Over-plotted is a calculation with exaggerated trial gas abundances of the undetected species to show their spectral signature (colored line). (b) & (d): the curve of growth of $\Delta \chi^2$ over a wide range of trial abundances. The 1, 2 and 3-$\sigma$ upper limits are indicated by the vertical dashed lines at $\Delta \chi^2 = 1, 4, 9$ respectively.