



COMMENT

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Key Points:

- We recover Venusian phosphine in SOFIA spectra by reducing contaminating signals; the PH₃ abundance is ~3 part-per billion (ppb)
- Six recoveries/limits show PH₃ depleting between clouds and mesosphere, which would require an unknown re-formation process or extra source
- Recoveries and upper limits can instead be reconciled by PH₃ photolysis, as high/low abundances correspond to Venusian mornings/evenings

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Comment on “Phosphine in the Venusian Atmosphere: A Strict Upper Limit From SOFIA GREAT Observations” by Cordiner et al.

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Abstract Searches for phosphine in Venus' atmosphere have sparked a debate. Cordiner et al. (2022, <https://doi.org/10.1029/2022gl101055>) analyze spectra from the Stratospheric Observatory For Infrared Astronomy (SOFIA) and infer <0.8 ppb of PH₃. We noticed that some spectral artifacts arose from non-essential calibration-load signals. By-passing these signals allows simpler post-processing and a 5.7 σ candidate detection, suggesting ~3 ppb of PH₃ above the clouds. Compiling six phosphine results hints at an inverted abundance trend: decreasing above the clouds but rising again in the mesosphere from some unexplained source. However, no such extra source is needed if phosphine is undergoing destruction by sunlight (photolysis), to a similar degree as on Earth. Low phosphine values/limits are found where the viewed part of the super-rotating Venusian atmosphere had passed through sunlight, while high values are from views moving into sunlight. We suggest Venusian phosphine is indeed present, and so merits further work on models of its origins.

Plain Language Summary Cordiner et al. (2022, <https://doi.org/10.1029/2022gl101055>) find no phosphine in Venus' atmosphere, using the airborne SOFIA telescope. By-passing some instrumental effects, we extract a detection with 5.7 σ -confidence from the same data. We can resolve the tension between high and low PH₃ abundance values by noticing that the former are from “mornings” in Venus' atmosphere and the latter from “evenings.” Sunlight reduces the amount of phosphine in Earth's atmosphere by an order of magnitude, so similarly on Venus, we might expect lower abundances in data taken when the part of the atmosphere observed has passed through sunlight. If the six available data sets can be reconciled in this way, further modeling of possible sources of PH₃ (e.g., volcanic, disequilibrium chemistry, extant life) seem worthwhile.

1. Introduction

Phosphine, if present in Venus' atmosphere, would be unexpected on an oxidized planet. Greaves et al. (2021) searched for PH₃ absorption at 1 mm wavelength, testing the concept that this molecule may be a biosignature when seen in anoxic environments. The unexpected detection-candidates from JCMT and ALMA have stimulated much community work on robust spectral processing, and on other methods to detect PH₃ at Venus, mostly proving negative except for an in situ mass-spectrometry recovery (Mogul, Limaye, Way, & Cordova, 2021). Particularly deep (above-cloud) limits have been set by infrared spectroscopy (Encrenaz et al., 2020; Trompet et al., 2020).

We comment here on the findings of Cordiner et al. (2022), hereafter C22, who present a deep upper limit from PH₃ observations with the GREAT instrument on SOFIA. They propose that all the candidate detections of phosphine in Venus' atmosphere could in fact be null results, given the complexity of the challenging observations—although their Figure 1 omits findings by Greaves et al. (2022), our work after calibration and contamination issues were fully resolved, where we find self-consistent 6–8 σ detections for the PH₃ $J = 1-0$ line from JCMT and ALMA.

The C22 observations are of the rotational transitions $J = 4-3$ and $2-1$ (around 1 and 0.5 THz), uniquely accessible to the SOFIA airborne telescope, and complementary to the existing $J = 1-0$ spectra (at 0.27 THz). From

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their $J = 4-3$ data processing, C22 find an upper limit of 0.8 ppb of PH_3 , applicable to most of the planet and 75+ km altitudes, while their $J = 2-1$ results suggest ~ 2.3 ppb could be present but only with 1.5σ confidence. These abundances are difficult to reconcile with ~ 20 ppb levels from the $J = 1-0$ data, without invoking strong temporal-variations or steep gradients over the slightly different altitudes these lines trace.

2. Materials and Methods

C22 note the existence in the GREAT spectra of quasi-periodic fringe patterns, due to standing waves between optical elements and to frequency-dependent gain factors used in calibration. Their calibration to antenna temperatures T_A follows the standard method of dividing the power difference of on- and off-Venus spectra by the power difference of hot and cold calibration-load signals, and then multiplying by the temperature difference of the hot and cold loads. We noticed that much of the fringing is introduced because the standing waves differ when observing the sky and the calibration loads. However, calibration to T_A is not essential here as we are only interested in measuring the line-to-continuum ratios, l/c , from which abundances derive (see e.g., Rezac et al. (2015) for analysis of l/c in SOFIA/GREAT data on Mars). In the case of the PH_3 $J = 4-3$ line components (seen by the “4G2 pixel”), an alternative is

$$l/c = (\text{On}_{\text{line}} - \text{Off}_{\text{line}}^*) / [0.5(\text{On} - \text{Off})] \quad (1)$$

where On and Off are the spectra on Venus and on adjacent blank sky, the subscript line indicates the broadband signals have been subtracted (using an automated all-band 4th-order polynomial fit), and $\text{Off}_{\text{line}}^*$ represents the instrumental line-signal that GREAT would see for a featureless patch of sky of similar brightness to Venus. $\text{Off}_{\text{line}}^*$ was generated by multiplying Off_{line} by a factor ~ 1.05 and adjusting this scalar until the residual ($\text{On}_{\text{line}} - \text{Off}_{\text{line}}^*$) was minimized—that is, the procedure tests the null hypothesis, that no absorbing gases are present. Applying a scale factor is the simplest possible approach to removing for example, residual slopes that may differ between On and Off. Smooth fits to On and Off (i.e., the 4th order polynomial fits) were used in the denominator of Equation 1 to avoid re-introducing noise that is already included in the numerator of Equation 1. The factor of 0.5 arises because GREAT is a double-sideband instrument with approximately equal sideband gains (see C22), and so records the planetary continuum twice. Equation 1 method has worked well here for PH_3 $J = 4-3$, reaching a similar noise level to C22, but our approach failed for the PH_3 $J = 2-1$ line-pair (“4G1 pixel”) because some sharp spike features in the spectra differ between On_{line} and Off_{line} .

Remaining ripples in the $J = 4-3$ spectra were then removed by a one-stage Fourier process, contrasting to the iterative 7-step Lomb-Scargle periodogram approach used by C22 (or traditional polynomial fitting, which is less useful for spectra with many ripples). Both we and C22 similarly “masked” the spectral regions where the four PH_3 components lie, to avoid fitting real lines as if they are ripples. C22’s periodogram method works intrinsically on masked data, while we interpolated across the line regions with quadratic fits anchored on adjacent spectral pixels. We used 3-sigma cuts in Fourier space, with features above these cuts inverse-Fourier-transformed to create a family of model sinusoids. Subtracting these model baselines yields well-flattened spectra (Figures 1a and 1b). Finally we “stack” the 24 samples of PH_3 absorption in the data (Figure 1c), namely from the 6 observations and their 4 spectral sections covering the $J = 4-3$ components, as these are of similar intrinsic line-depth (see Figure 3 in C22). Two of the PH_3 features are close together (Figure 1b), and so to avoid adjacent features appearing again but off-center, we replaced these sections of data (for simplicity, flipping the data on the spectral axis so that a line-free section can be swapped in as replacement noise), before making the final stack.

Several robustness checks were run, exploring possible processing issues.

- The net result could be dominated by a few strong artifacts, causing a net “fake line” even if most of the 24 samples were null. This was found not to be the case, with the line-integrals from the 24 samples following an approximately normal (Gaussian) distribution with no outliers above 2σ . The result is also robust to removing a few points. For example, the final observation (#040402) was the noisiest, and removing all these samples from the stack shifts the net line-integral by only -20% .
- There could be terrestrial atmospheric signals in the band, that affect the validity of minimizing the numerator in Equation 1; in particular, C22 note two frequencies where there may be O_3 and N_2O absorption (at 1,078.686 and 1,078.621 GHz, i.e., contamination from the opposite sideband). We re-calculated the scalar used in Equation 1 with the O_3 and N_2O regions blanked, and found negligible change (noise reduction of around 1%).

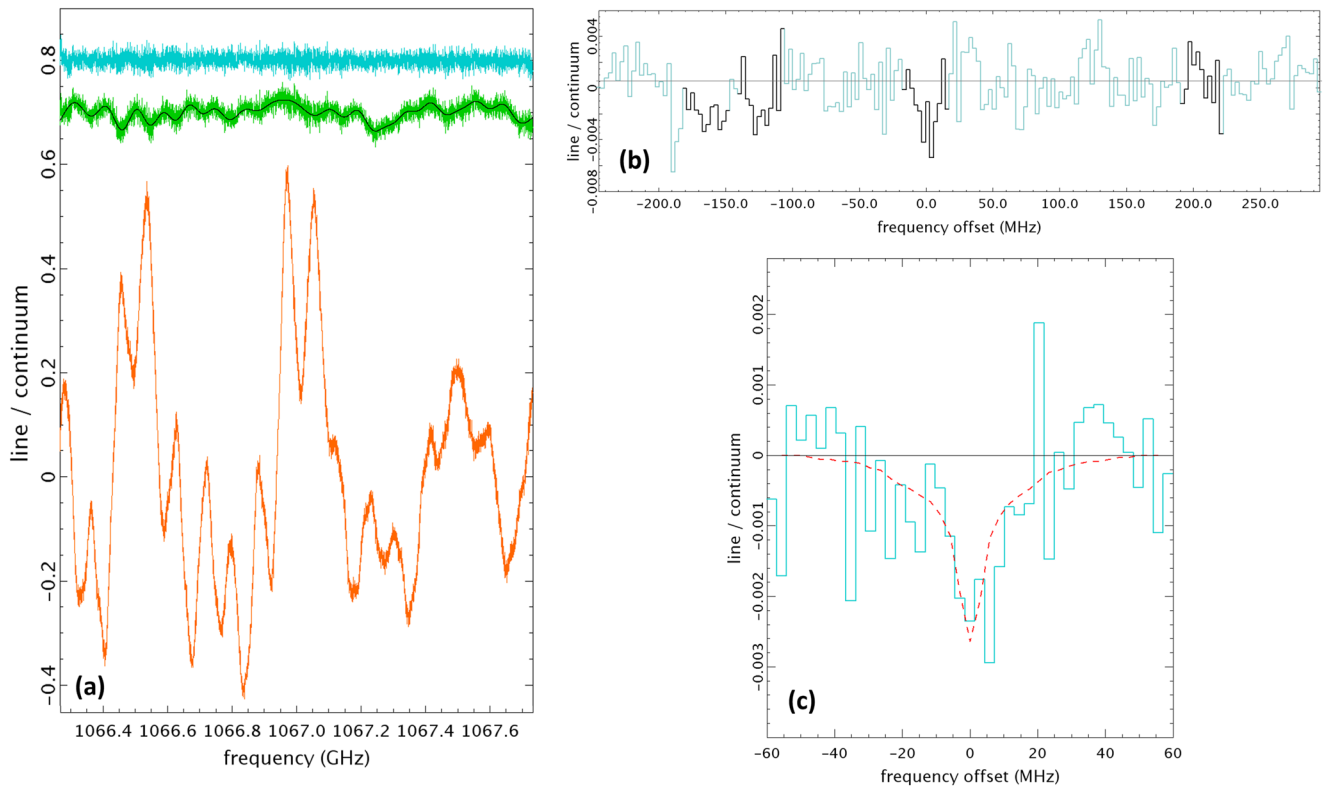


Figure 1. The process of extracting the PH_3 , $J = 4-3$ signal from the GREAT data is illustrated. Panel (a) illustrates processing of 6,000 spectral pixels from observation #040093 from the first SOFIA flight (vertical offsets are for clarity only). The lower orange histogram (bar graph) is from a standard On-Off processing; the middle green histogram is the result after applying the Equation 1 step, and is overlaid with the Fourier-derived trend (black curve); the top blue histogram is the flattened output after subtracting this trend. In panel (b), the blue histogram is the unweighted average of all six observations made over the three flights, with the sections centered on the frequencies of the four PH_3 , $J = 4-3$ components highlighted in black. Frequency offset is referenced to the component at 1,067.0003 GHz. Models predict that the four components have the same profiles and similar line-depths ($\pm 20\%$ deviations from the mean). The spectral pixels are binned in groups of 12 in (b) and (c) to improve clarity, and the thin black line shows the zero-level correction made between (b) and (c). Panel (c) shows (blue histogram) the unweighted stack of all 24 spectral sections containing PH_3 , $J = 4-3$ features. The dashed red curve is a model for 3 ppb of phosphine, generated vis the Planetary Spectrum Generator (PSG) (<https://psg.gsfc.nasa.gov/index.php>) following C22. The four line-components from the PSG model were masked and stacked similarly to the data.

- The interpolation across the PH_3 line-regions might not be following the correct trend, potentially always producing negative residuals that mimic absorption lines. We tested this by re-running the processing identically, but shifting the spectral sections to parts of the band without phosphine features. From 50 tests, none produced a result like Figure 1c, namely a “fake” absorption that is the only feature, centrally placed, and of comparable width to line models (see below).

3. Results

Three of the four expected PH_3 , $J = 4-3$ components are recovered when all the observations are co-added (Figure 1b), while only one component was apparent in Figure 3 of C22. In Figure 1c, our final stacked spectrum indicates an overall 5.7σ detection of PH_3 , $J = 4-3$, when integrated over ± 17 MHz (the masked region). This confidence level changes marginally (by $\pm 0.4\sigma$) if a different range of spectral pixels is used to calculate the zero-level.

We then modeled our net spectrum using the same online tool as C22. We ran a model for 1 ppb of phosphine and scaled it linearly for different abundances, and then calculated a reduced-chi-squared statistic to assess goodness of fit. Figure 1c illustrates that 3 ppb of PH_3 provides a good match to the observed line, with χ^2_r of 0.75. (The uncertainties used in χ^2_r were generated per spectral pixel from the internal data dispersion.) We consider that fitting the stacked spectrum better mitigates against artifacts, compared to matching the individual components (Figure 1b) against the model. For example, inserting a single positive “spike” near the highest-frequency

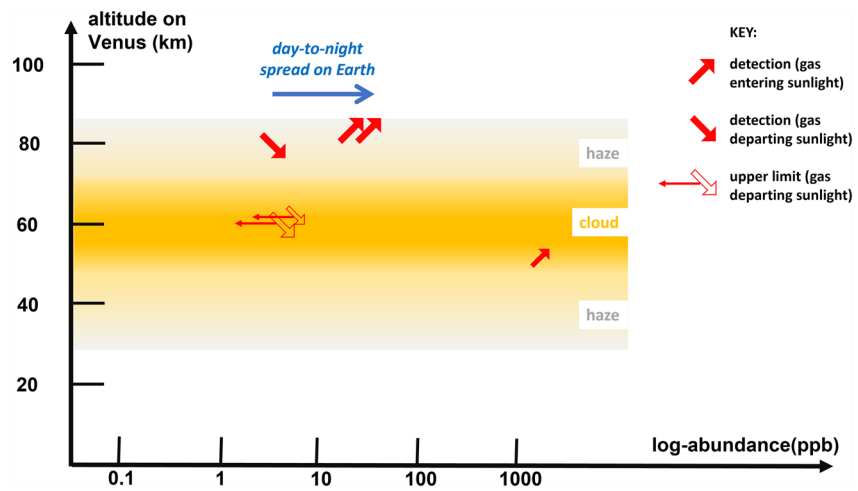


Figure 2. The trend of phosphine abundances by altitude is sketched. Symbols indicate candidate detections plus best upper limits for phosphine abundances. Rising arrows indicate observations made where the super-rotating atmosphere was rising into sunlight and falling arrows indicate observations made where the atmosphere was descending toward the nightside (see key). Large and small symbols indicate that a large fraction of the planet area was observed, or that a small region was sampled, respectively. Abundance estimates are, from top: ~ 20 , 25 ppb from $J = 1-0$ data (via (Greaves et al., 2022) and with altitude proposed by C22); 3 ppb from $J = 4-3$ data (this work; beam centered on the evening side); < 7 ppb at 62 km from 4 μm spectra (Trompet et al., 2020: low-latitude data to best match whole-planet studies); < 5 ppb at 60 km from 10 μm spectra (Encrenaz et al., 2020: latitudes within $\pm 50^\circ$); ~ 2 ppm at 51 km from Pioneer-Venus in situ sampling during descent (Mogul, Limaye, Way, & Cordova, 2021). The blue arrow indicates the ten-fold increase of terrestrial phosphine from day to night (Glindemann et al., 1996)—note the arrow's plotted position is arbitrary; Earth hosts much lower PH_3 than Venus.

component (Figure 1b) was found to significantly reduce the inferred PH_3 abundance, as the χ^2 test attempts to minimize the discrepancy of positive data against a negative model-line. As a positive feature does appear here in this part of C22's spectrum (their Figure 3), this could have driven their upper limit down to the ≤ 0.8 ppb they obtain. However, we do not rule out an abundance as low as 0.8 ppb, which is at the lower 99% confidence-bound in our χ^2 tests. We also note that C22 estimated ~ 2.3 ppb from their PH_3 $J = 2-1$ spectrum, albeit at only $+1.5\sigma$ confidence, and this estimate is compatible with our 3 ppb result.

C22 (Figure S4) find that altitudes around ~ 80 km are the best-sampled at the PH_3 $J = 4-3$ line-frequency; our recovery here is consistent with the model that we both use, and with the predicted short lifetime of PH_3 above ~ 80 km (Bains, Petkowski, Seager, et al., 2021). Altitudes are however uncertain because the PH_3 - CO_2 pressure-broadening coefficient has not been experimentally verified. We also note that all GHz/THz data are limited by the spectral span that can be recovered. Here, any absorption wider than ~ 200 MHz leads to merged PH_3 $J = 4-3$ components, and so any phosphine signatures below ~ 70 km (roughly cloud-top level) are lost.

4. Discussion

Debates continue about the best methods to acquire and process deep GHz/THz spectra of Venus. These observations are very challenging in dynamic range, as Venus is so bright, revealing “ripples” in spectral baselines that are not evident in more typical telescope usage. Depending on preferred approaches, different authors argue for between zero and three published detections of rotational (J) transitions of PH_3 .

We can compare results from the data discussed here with the outcomes of other searches for phosphine at Venus, and assess whether this results in a plausible altitude profile of the molecule (Figure 2). The trend found by connecting the results from six searches for phosphine appears as an upwards decline that then reverses, that is, PH_3 that is depleted somewhere between ~ 50 and ~ 80 km. This is hard to explain in the absence of a chemical route to reform the molecules, or a new mesospheric source. The order-of-magnitude contrast between some of the candidate detections and the upper limits has led to doubts over the presence of phosphine (see e.g., the recent summary in Clements (2023), Mogul, Limaye, Lee, and Pasillas, (2021), and Mogul, Limaye, Way, and Cordova, (2021) for the PH_3 recovery from data taken by the Pioneer-Venus descent probe in 1978).

However, we noticed that this divide is also between observations made when the “morning” versus the “evening” sides of Venus' atmosphere were targeted—and this is relevant in gas-mixing processes (e.g., Lefèvre et al., 2022). Where the gas observed on Venus has traveled through sunlight and is descending toward the night-side of the planet, we detect at most the ~ 3 ppb of phosphine estimated here. In contrast, where gas is rising into sunlight, we observe $\geq \sim 20$ ppb of PH_3 . Hence photolysis—similar to the observed destruction of terrestrial phosphine by sunlight (Sousa-Silva et al., 2020)—could explain the split between high and low phosphine abundances observed on Venus. It is striking that this evening/morning difference is comparable in magnitude to the factor ~ 10 difference over night/day for phosphine in the Earth's atmosphere (Glindemann et al., 1996; noting absolute abundances are much lower on Earth).

5. Conclusions

The question regarding phosphine in Venus' atmosphere is likely to be debated for some time. A further JCMT survey is ongoing (see <https://www.eaoobservatory.org/jcmt/science/large-programs/jcmt-venus-monitoring-phosphine-and-other-molecules-in-venus-atmosphere/>; PI. D. Clements) and is producing open-source data that should yield more definitive answers—in particular, that team is now processing broadband spectra that can sample the cloud decks. The most direct answer regarding phosphine could come from new in situ sampling, potentially with the addition of one laser channel to the Venus Tunable Laser Spectrometer (VTLS) instrument on-board the DAVINCI descent probe (Garvin et al., 2022).

The origins of any phosphine present are also debated, and most scenarios are hard to test for lack of some contextual data. For example, it seems only extraordinary volcanic activity could make \sim ppb-level phosphine (Bains et al., 2022) but volcanism on Venus is not well understood. In some new avenues, (Ferus et al., 2022) discuss abiotic routes to phosphine involving redox disequilibrium, while others (Bains, Petkowski, Rimmer, & Seager, 2021; Mogul, Limaye, Lee, & Pasillas, 2021) explore phototrophic life and the habitability of the clouds. We conclude that establishing an improved PH_3 altitude-profile is worthwhile to test these new models of origins.

Data Availability Statement

The SOFIA Level 1 data are available under project id 75_0059_1 through the public data archive at <https://irsa.ipac.caltech.edu/applications/sofia>. The custom software to generate the data shown in the figures is supplied at <https://doi.org/10.5281/zenodo.8063984>. This plain-text script includes comments on all the processing described here. The script requires the UK-Starlink software (Currie et al., 2014) which is currently supported by the East Asian Observatory and available at <https://starlink.eao.hawaii.edu/starlink/2021ADownload>.

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