

Phosphine Gas in the Cloud Decks of Venus

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Measurements of trace-gases in planetary atmospheres help us explore chemical conditions different to those on Earth. Our nearest neighbor, Venus, has cloud decks that are temperate but hyper-acidic. We report the apparent presence of phosphine (PH₃) gas in Venus' atmosphere, where any phosphorus should be in oxidized forms, based on single-line millimeter-waveband spectral detections (quality up to $\sim 15\sigma$) from the JCMT and ALMA telescopes. Atmospheric PH₃ at ~ 20 parts-per-billion abundance is inferred. There is no other plausible line-identification, and exhaustive study of steady-state chemistry and photochemical pathways finds no viable abiotic phosphine-production routes in the atmosphere, clouds, surface and subsurface, nor from lightning, volcanic or meteoritic delivery. Phosphine could originate from unknown photochemistry or geochemistry, or, by analogy with biological production of phosphine on Earth, from the presence of life. Other PH₃ spectral features should be sought, while future in-situ cloud and surface sampling could examine sources of this gas.

Studying rocky-planet atmospheres gives clues to how they interact with surfaces and subsurfaces, and whether any non-equilibrium compounds could reflect the presence of life. Characterizing extrasolar-planet atmospheres is extremely challenging, especially for rare compounds¹. The solar system thus offers important testbeds for exploring planetary geology, climate and habitability, via both *in-situ* sampling and remote-monitoring. Proximity makes signals of trace gases much stronger than those from extrasolar planets, but issues remain in interpretation.

Thus far, solar system exploration has found compounds of interest, but often in locations where the gas-sources are inaccessible, such as the Martian sub-surface² and water-reservoirs inside icy moons^{3,4}. Water, simple organics and larger unidentified carbon-bearing species⁵⁻⁷ are known. However, geochemical sources for carbon-compounds may exist⁸, and temporal/spatial anomalies can be hard to reconcile, e.g. for Martian methane sampled by rovers and observed from orbit⁹.

An ideal biosignature-gas would be unambiguous. Living organisms should be its sole source, and it should have intrinsically-strong, precisely-characterized spectral transitions unblended with contaminant-lines – criteria not usually all achievable. It was recently proposed that any phosphine detected in a rocky-planet's atmosphere is a promising sign of life¹⁰. Trace PH₃ in the Earth's atmosphere (parts-per-trillion abundance globally¹¹) is uniquely associated with anthropogenic activity or microbial presence – life produces this highly-reducing gas even in an overall oxidizing environment. Phosphine is found elsewhere in the solar system only in the reducing atmospheres of giant planets^{12,13}, where it is produced in deep atmospheric layers at high temperatures and pressures, and dredged upwards by convection^{14,15}. Solid surfaces of rocky planets present a barrier to their interiors, and phosphine would be rapidly destroyed in their highly-oxidized crusts and atmospheres. Thus PH₃ meets most criteria for a biosignature-gas search, but is challenging as many of its spectral features are strongly absorbed by the Earth's atmosphere.

Here we exploit the PH₃ 1-0 millimeter-waveband rotational-transition that could absorb against optically-thick layers of Venus' atmosphere. Our motivation was long-standing speculation regarding an aerial biosphere in the high-altitude cloud decks^{16,17}, where conditions have some similarity to ecosystems making phosphine on Earth¹⁸. We exploited good instrument sensitivity, 25 years after the first millimeter-waveband exploration of solar-system PH₃ (in Saturn's atmosphere¹⁹). We proposed a 'toy-model' experiment that could set abundance-limits of order parts-per-billion on Venus, comparable to phosphine production of some anaerobic Earth ecosystems¹⁰. The aim was a benchmark for future developments, but unexpectedly, our initial observations suggested a detectable amount of Venusian phosphine was present.

We present next the discovery data, confirmation (and preliminary mapping) by follow-up observations, and rule out line-contamination. We then address whether gas reactions, photo/geochemical reactions or exogenous non-equilibrium input could plausibly produce PH₃ on Venus.

Results

The PH₃ 1-0 rotational transition at 1.123 mm wavelength was initially sought with the James Clerk Maxwell Telescope (JCMT), in observations of Venus over 5 mornings in June 2017. The single-point spectra cover the whole planet (limb down-weighted by ~50% within the telescope

beam). Absorption lines from the cloud decks were sought against the quasi-continuum created by overlapping broad emission features from the deeper, opaque atmosphere.

The main limitation at small line-to-continuum ratio (hereafter, l:c) was spectral ‘ripple’, from artefacts such as signal reflections. We identified three issues (see Supplementary Information (SI): JCMT data analysis), with the most-problematic being high-frequency ripple drifting within observations in a manner hard to remove even in Fourier space (Fig. S1). We thus followed an approach standardised over several decades²⁰, fitting amplitude-versus-wavelength polynomials to the ripples (in 140 spectra). The passband was truncated to 100 km/s to avoid using high polynomial-orders. (Order is based on the number N of ‘bumps’ in the ripple-pattern; fitting is optimal with order N+1 and negligibly improved at increased order. A wider band includes more ‘bumps’, increasing N. For minimum freedom, a linear fit can be employed immediately around the line-candidate, ignoring the remaining passband – see Table 1 for resulting systematic differences.) We explored a range of solutions with the spectra flattened outside a velocity-interval within which absorption is allowed. (The polynomial must be interpolated across an interval, since if fitted to the complete band it will always remove a line-candidate, given freedom to increase order.) These interpolation-intervals ranged from very narrow, preserving only the line core (predicted by our radiative-transfer models, Fig. 1), up to a Fourier-defined limit above which negative-sign artefacts can mimic an absorption line. Details are in SI: JCMT data analysis (with the reduction script appended). The spectra were also reduced completely independently by a second team member, via a minimal-processing method that collapses the data-stack down the time-axis and fits a one-step low-order polynomial; this gave a similar output-spectrum but with lower signal-to-noise.

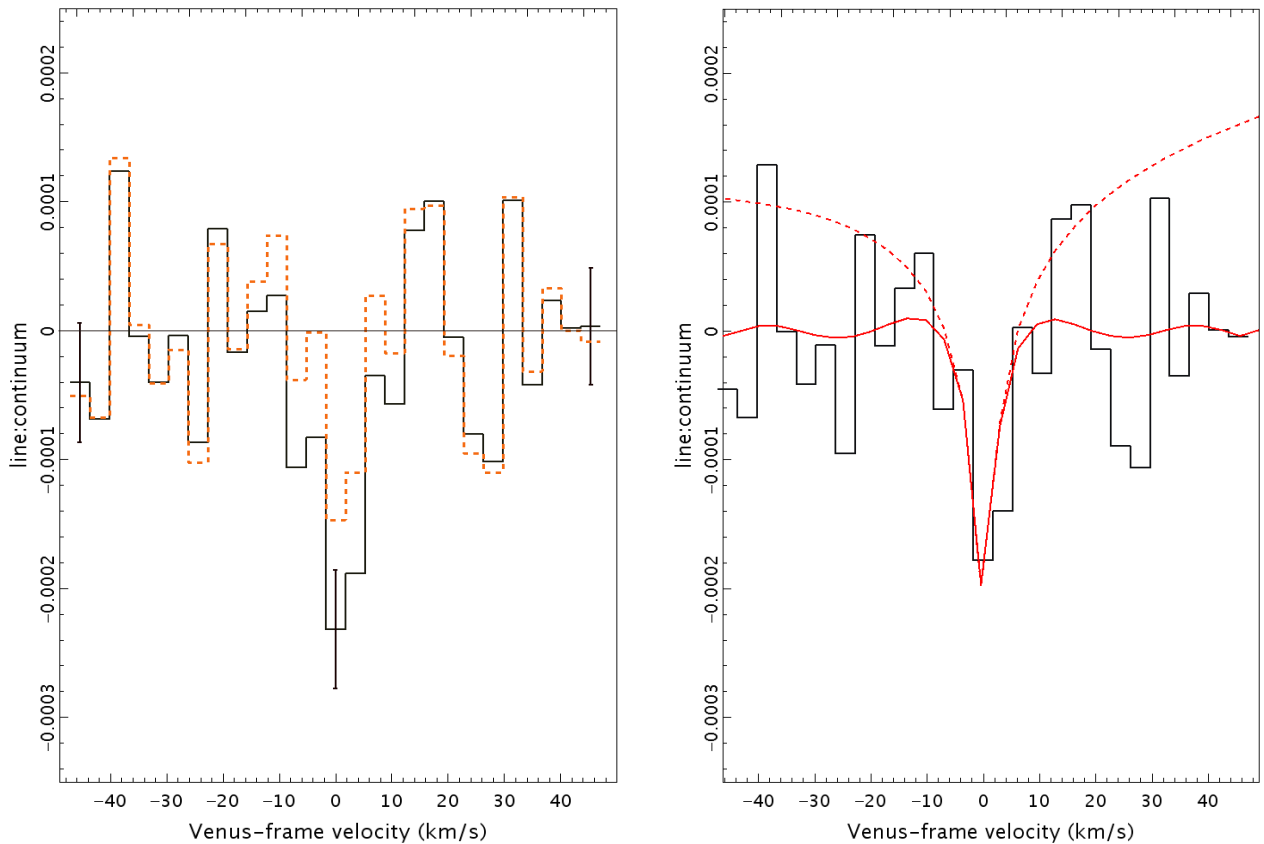


Fig. 1. Panels show spectra of PH₃ 1-0 in Venus' atmosphere as observed with the JCMT. Axes are line-to-continuum ratio against Doppler-shifted velocity referenced to the phosphine wavelength. Left: the least and most conservative solutions after fitting and removing spectral ripple (see SI: JCMT data analysis), with the residual line present inside velocity-ranges of $|v| = 8$ km/s (solid, black) and $|v| = 2$ km/s (dashed, orange). The data have been binned into histograms (bars denoting averages) on the x-axis for clarity; representative 1σ error bars are $0.46 \cdot 10^{-4}$ in l:c per 3.5 km/s spectral bin. Error bars indicate the dispersion within each channel from 140 co-added input spectra; channel-to-channel dispersion is higher by $\sim 40\%$, attributable to residual ripple, and contributing to the range of signal-to-noise (Table 1). Right: the adopted mid-range solution with $|v| = 5$ km/s (histogram), overlaid with our model for 20 ppb abundance-by-volume. The solid red curve shows this model after processing with the same spectral fitting as used for the data. The line wings and continuum slope have thus been removed from the original model (upper dashed red curve). As the spectral fitting forces the line wings towards zero, only the range ± 10 km/s around Venus' velocity was used in line characterisation (Table 1).

In our co-added spectrum (Fig. 1), we saw candidate PH₃ 1-0 absorption, with signal-to-noise varying over $\sim 3-7$, depending on the velocity-interval selection. The feature is consistent with Venus' velocity, but is not precisely characterized (Table 1). This potentially allows for the feature to be a weak residual artefact, or a transition of another molecule at a nearby wavelength.

We thus sought confirmation of the same transition, with independent technology and improved signal-to-noise, using the Atacama Large Millimetre/submillimetre Array (ALMA) in March 2019. In principle, ALMA's arcsecond-scale resolution would allow detailed mapping of the planet's atmosphere. In practice, interferometric response to a large bright planet produced artefactual spectral ripples varying from baseline to baseline (and not eliminated by bandpass calibration). This systematic was greatly reduced, prior to imaging, by excluding all telescope-to-telescope baselines < 33 m in length. This was necessary for dynamic range and was the only significant departure from the standard ALMA 'QA2' approach²¹ to data reduction (see SI: ALMA data analysis; Figs S2, S3; appended reduction-scripts). While bandpass calibration using Jupiter's moon Callisto was not fully sufficient, the dynamic range achieved was still substantially higher than ALMA's specification ($\sim 10^{-3}$ in l:c, without the techniques we used to reduce systematics, and which we verified did not produce spurious features). To eliminate residual ripple from the extracted spectra, we tested polynomial-fitting strategies with orders ranging from 12 (optimal for an 80 km/s passband, Figs. 2, S4), down to 1 (fitting only around the line-candidate). The resulting systematic uncertainties are summarised in Table 1.

We also checked for robustness by searching simultaneously for deuterated water (HDO) known to be present on Venus. The HDO $2_{2,0}-3_{1,3}$ line at 1.126 mm wavelength was detected (Fig. S5: preliminary output from manual 'QA2' scripts), with a line profile well-fitted by our radiative transfer model, and a Venus-normal water abundance (see SI: ALMA data analysis). Simultaneous wider-bandpass settings also allowed us to set upper limits on other chemical species – transitions here could be a check on possible contaminants, i.e. constrain transitions close in wavelength to the line we identify as PH₃ 1-0. The wide-bandpass tuning centred on this PH₃ transition provided a further reproducibility check. These data have significantly greater problems with spectral ripple than in the narrow-bandpass settings, but the phosphine line was recovered (Fig. S6).

The effect of removal of short-baseline ALMA data is that line-signals from areas smooth on scales > 4 arcseconds are substantially diluted. Thus our l:c correspond to lower limits of PH_3 abundance (but detection-significance is not affected; these values are as stated in Table 1). Further, the steep flux density gradients at the limb resulted in more flux being recovered here.

5 To ensure that results are robust, we did not attempt to interpret any absorption spectra over arcsec-scales (see Fig. S3). To mitigate for the bias in better-sampling the limb, the spectra in Figure 2 are all averages from ‘side-to-side’ strips across the planet.

The ALMA data confirm the detection of absorption at the PH_3 1-0 wavelength. All line-centroid velocities are consistent with Venus’ velocity within -0.2 to $+0.7$ km/s (around 10% of the line width), with best measurement-precision at ± 0.3 km/s and systematics of ~ 0.1 - 0.7 km/s (Table 1). For this degree of coincidence of apparent velocity, any contaminating transition from another chemical species would have to coincide in rest-wavelength with PH_3 1-0 within $\sim 10^{-6}$.

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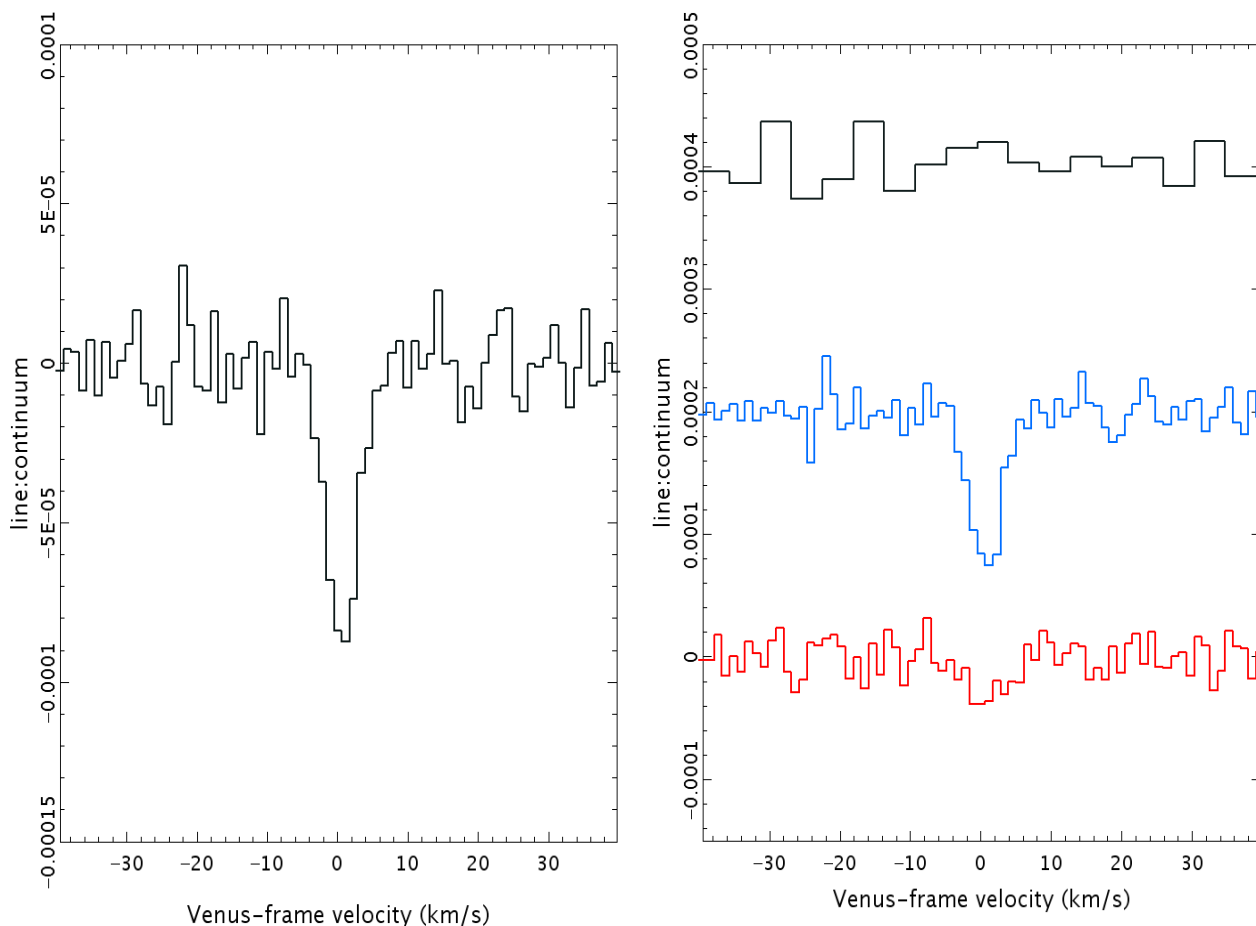


Fig. 2. Spectra of Venus obtained with ALMA, in the same format as Fig. 1. Left panel shows the PH_3 1-0 spectrum of the whole planet, with 1σ errors (here channel-to-channel) of $0.11 \cdot 10^{-4}$ per 1.1 km/s spectral bin. Right panel shows spectra of the polar (histogram in black), mid-latitude (in blue) and equatorial (in red) zones, as defined in Table 1. Spectra have been offset vertically for clarity, and the polar spectrum was binned in velocity to obtain a deeper upper limit. Line wings are forced towards zero outside $|v| = 5$ km/s in these spectra, and only this range was used in characterization (Table 1; SI: ALMA data analysis).

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facility (epoch)	area of planet	line-to-continuum ratio (10^{-4})	centroid (km/s)	FWHM (km/s)	signal-to-noise ratio	Notes
JCMT (June, 2017)	whole planet	-2.5 ± 0.8 (-2.2, -3.1)	-0.2 ± 1.1 (-0.3 \pm 1.2, -0.3 \pm 0.9)	3.6 ± 1.2 (2.8 \pm 1.0, 8.2 \pm 2.3)	4.3 (3.0, 6.7)	$ v = 5$ km/s ($ v = 2,8$ km/s for systematics)
ALMA (March, 2019)	whole planet	-0.87 ± 0.11	$+0.7 \pm 0.3$ (+0.3 \pm 0.3)	4.1 ± 0.5	13.3	$ v = 5$ km/s (linear fit for systematic)
	equator (15°S-15°N)	-0.39 ± 0.14	$+0.7 \pm 0.9$ (-0.0 \pm 0.4)	4.8 ± 1.8	5.0	as for whole planet
	mid-latitude (15-60°S + 15-60°N)	-1.26 ± 0.14	$+0.7 \pm 0.3$ (+0.4 \pm 0.3)	4.1 ± 0.6	14.5	as for whole planet
	polar (60-90°S + 60-90°N)	(3 σ : -0.29)	---	---	---	limit for 10 km/s bins

Table 1. Properties of the absorption line for regions of Venus' atmosphere. Measurement errors are 1σ , and systematic errors are differences of the means and the mean values in brackets, the latter being obtained with the data-processing modifications stated in the ‘Notes’ column. Line-to-continuum ratios are measured at line-minimum, for 1.1 km/s spectral bins that are in common to both datasets. Centroid velocities are referenced to the PH₃ 1-0 line-identification. Lines were fitted with Lorentzian profiles over ± 10 km/s to estimate full-width half-minima (FWHM). For JCMT, intensity-weighted velocity centroids and line-integrated signal-to-noise (based on per-channel errors) were calculated over ± 10 km/s velocity-ranges. For ALMA, calculation ranges were restricted to ± 5 km/s because of complexity of spectral ripple (see Fig. S4), and centroids in brackets are for comparison, from a simplified linear fit immediately adjacent to the absorption. In all other cases, the results are from the spectra in Figures 1 and 2, after the removal of polynomial baselines of order 8 (JCMT) and 12 (ALMA). We verified that high-order fitting does not produce artefact lines at arbitrary positions in the passband (Figs. 3, S4).

The data above represent the candidate discovery of phosphine on Venus. Because of the very high l:c sensitivity required, we tested robustness through several routes. In particular, we analysed data from both facilities by a range of methods and estimated systematic uncertainties.

The JCMT and ALMA whole-planet spectra agree in line-velocity and width, and are consistent in line-depth after taking into account ALMA’s spatial filtering (hence, no temporal-variation in PH₃ abundance needs to be invoked over 2017-2019). We considered ALMA’s maximum line-loss, in the case of a phosphine distribution as uniform as the almost-smooth continuum (Fig. S2). Comparing the ALMA continuum signals with/without baselines of < 33 m in the data reduction, we found filtering-losses varying from a net 60% in our polar regions to 92% for our equatorial band. Correcting the whole-planet line-signal by this method, l:c could rise from $-0.9 \cdot 10^{-4}$ to $-4.9 \cdot 10^{-4}$, values bracketing $-2.5 \cdot 10^{-4}$ from the JCMT. Hence, the ALMA and JCMT lines differ by factors of at most 2-3, with agreement possible if the phosphine is distributed on intermediate scales (between highly-uniform and small patches).

Finally, for robustness, we considered the possibility of a ‘double-false-positive’, where a negative-dip occurs in both datasets near the Venusian velocity. Comparing the data *before* the final processing-step of polynomial-fitting take place, Figure 3 shows that no other coincidences of absorption-line-like features occur in the JCMT and ALMA spectra.

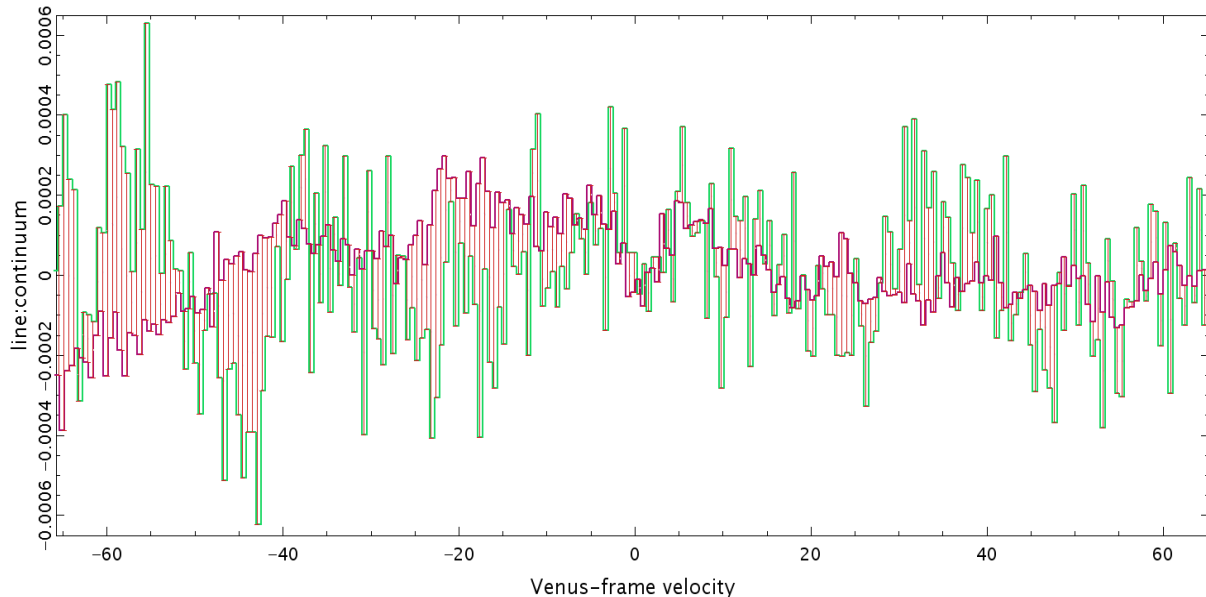


Fig. 3. JCMT and ALMA whole-planet spectra (green and purple histograms, respectively), across the full passband in common. These are the co-added spectra *before* the removal of a final polynomial baseline. The ALMA spectrum has been scaled up by a factor of 3, the estimated loss for spatial filtering (compare the first two l:c entries in Table 1). Vertical red bars connect the JCMT and ALMA data (their spectral bin-centres agree in velocity within ± 0.2 km/s). A line feature is considered to be real where this dispersion (red bar) is low, and only the candidate phosphine feature around $v = 0$ km/s meets this criterion. Other candidate ‘dips’ across the band have high dispersion (as they occur only in one dataset), or cover only a few contiguous bins (much less than the line-width expected for Venusian upper-atmosphere absorption).

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Next, we examined whether transitions from gases other than PH_3 might absorb at nearby wavelengths. The only plausible candidate (Table S1) is an SO_2 transition offset by $+1.3$ km/s in the reference frame of PH_3 1-0. This is expected to produce a weak line in the cloud decks, with its lower quantum-level at energy > 600 K not being highly-populated in < 300 K gas. SO_2 absorptions from energy-levels at ~ 100 K have been detected²², and we searched for one such transition in our simultaneous ALMA wideband-data. We did not detect significant absorption (Figure 4). Given this observation, our radiative-transfer model predicts what the maximum absorption from the ‘contaminant’ SO_2 line would be, finding a weak l:c, not deeper than $-0.2 \cdot 10^{-4}$ (Figure 4). SO_2 can contribute a maximum of $< 10\%$ to the l:c integrated over ± 5 km/s, and shift the line-centroid by < 0.1 km/s. These results are abundance- and model-independent. The contaminant- SO_2 -line could only ‘mimic’ the phosphine feature while the wideband- SO_2 -line remained undetected if the gas were more than twice as hot as measured in the upper clouds – i.e. at temperatures only found at much lower altitudes than our data probe.

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We are unable to find another chemical species (known in current databases) besides PH_3 that can explain the observed features. We conclude that the candidate detection of phosphine is robust, for four main reasons. Firstly, the absorption has been seen, at comparable line depth, with two independent facilities; secondly, line-measurements are consistent under varied and independent processing methods; thirdly, overlap of spectra from the two facilities shows no other such consistent negative features; and fourthly, there is no other known reasonable candidate-transition for the absorption other than phosphine.

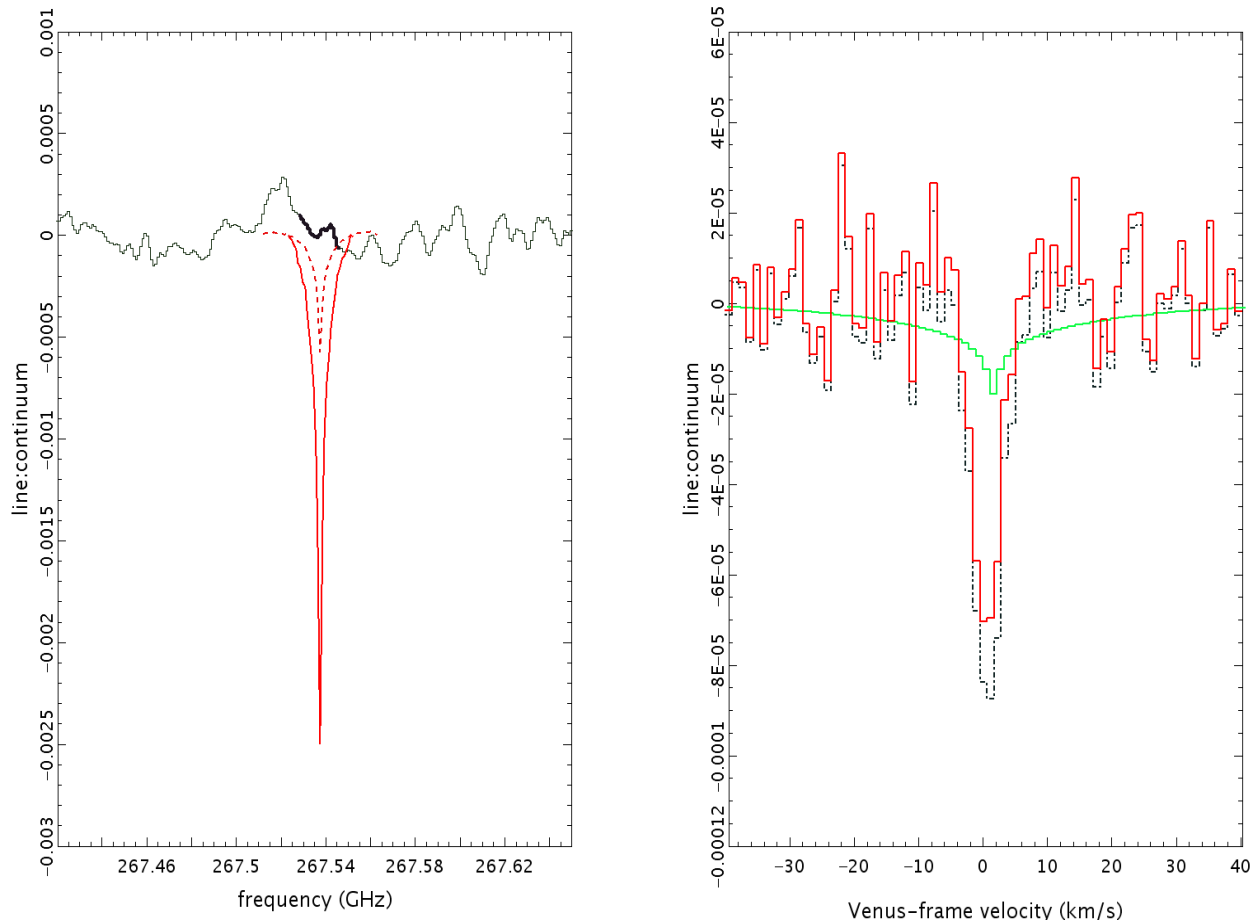


Fig. 4. Left panel shows a section of ALMA wideband data (whole planet, after a 3rd-order polynomial correcting for broad curvature has been removed), around the SO₂ 13_{3,11}-13_{2,12} rest-frequency (267.53745 GHz; wavelength \approx 1.121 mm). The thicker histogram over ± 10 km/s range illustrates that SO₂ absorption is not seen. The red dashed curve is an SO₂-10 ppb model, after subtracting a polynomial forcing line wings towards zero outside $|v| = \pm 10$ km/s. The 10 ppb model was chosen to reproduce the maximum line depth possible within the data, approximating to the peak-to-peak spectral ripple. The red solid curve is scaled up to show the amplitude this SO₂ line would need to have if the line we identify as PH₃ 1-0 is instead all attributed to the SO₂ 30_{9,21}-31_{8,24} transition. Right panel re-plots our model for the maximum allowed SO₂ 30_{9,21}-31_{8,24} contribution (as in the red dashed model of the left panel, but without the polynomial subtraction: green histogram). The PH₃ whole-planet spectrum (black dot-dashed histogram) is then re-plotted (red solid histogram) after subtraction of this maximized level of SO₂ 30_{9,21}-31_{8,24}.

The few-km/s widths of the PH₃ spectra are typical of molecular absorptions from the upper atmosphere of Venus²². Inversion techniques²⁷ could convert the PH₃ line-profiles into a vertical molecular-distribution, but this is challenging here due to uncertainties in line-dilution and pressure-broadening. As the continuum against which we see absorption²⁸ arises at altitudes ~ 53 -61 km (Fig. S2), in the middle/upper cloud deck layers¹⁷, the PH₃ molecules observed must be at least this high up. Here the clouds are ‘temperate’, at up to $\sim 30^\circ\text{C}$, and with pressures up to ~ 0.5 bar²⁹. However, phosphine could form at lower (warmer) altitudes and then diffuse upwards.

Phosphine is detected most strongly at mid-latitudes, and is not detected at the poles (Table 1). The equatorial zone appears to absorb more weakly than mid-latitudes, but equatorial and mid-latitude values could agree if corrections are made for spatial filtering. Following the method above (treating gas as if distributed like the continuum), then l:c can be as deep as $-4.6 \cdot 10^{-4}$ for the equator and $-5.8 \cdot 10^{-4}$ for mid-latitudes, in agreement at the 1σ bounds (both $\pm 0.7 \cdot 10^{-4}$). However, for the polar caps, l:c cannot exceed $-0.7 \cdot 10^{-4}$ by this method (as small limb regions are the least-affected by missing short-baseline data). Our latitude ranges were set empirically, to maximise contrasts in l:c, so may not represent physical zones. We were unable to compare bands of longitude (e.g. for any effects of Solar angle), as regions nearer the limb had increasing issues of noise and spectral ripple (Fig. S3).

The abundance of phosphine in Venus' atmosphere was estimated by comparing a model line to the JCMT spectrum, which has the least signal-losses. The radiative transfer in Venus' atmosphere was calculated using a spherical, multi-layered model, with temperature and pressure profiles from the Venus international reference atmosphere (VIRA). Molecular absorptions are calculated by a line-by-line code, including CO₂ continuum-induced opacity. JCMT beam-dilution is included. The abundance calculated is ~ 20 ppb (Figure 1). The model's major uncertainty is in the CO₂ pressure-broadening coefficient, which has not been measured for PH₃. We take PH₃ 1-0 line broadening coefficients to range from $0.186 \text{ cm}^{-1}/\text{atm}$, (our theoretical estimate) to $0.286 \text{ cm}^{-1}/\text{atm}$ (the measured value for the CO₂ broadening of the NH₃ 1-0 line). Ammonia and phosphine share many similarities (see SI: Abundance retrieval), and can be expected to have comparable broadening properties^{30,31}. With this range of coefficients, derived abundances range from ~ 20 ppb (using our theoretical estimate) up to ~ 30 ppb (using the proxy NH₃-broadening). Additionally, uncertainty in l:c in the JCMT spectrum contributes $\sim 30\%$ (± 6 ppb), with additional shifts of $-2, +5$ ppb possible from systematics (Table 1).

The presence of even a few parts-per-billion of phosphine is completely unexpected for an oxidized atmosphere (where oxygen-containing compounds greatly dominate over hydrogen-containing ones). We review all scenarios that could plausibly create phosphine, given established knowledge of Venus.

The presence of PH₃ implies an atmospheric, surface or subsurface source of phosphorus, or delivery from interplanetary space. The only measured values of atmospheric P on Venus come from Vega descent probes³², which were only sensitive to phosphorus as an element, so its chemical speciation is not known. No P-species have been reported at the planetary surface.

The bulk of any P present in Venus' atmosphere or surface is expected as oxidized forms of phosphorus, e.g. phosphates. Considering such forms, and adopting Vega abundance data (the highest inferred value, most favorable for PH₃ production), we calculate whether equilibrium thermodynamics under conditions relevant to the Venusian atmosphere, surface, and subsurface can provide ~ 10 ppb of PH₃. (We adopt a lower-bound adequately fitting the JCMT data, to find the most readily-achievable thermodynamic solution.) We find that PH₃ formation is not favored even considering ~ 75 relevant reactions under thousands of conditions encompassing any likely atmosphere, surface, or subsurface properties (with temperatures of 270-1500 K, atmospheric and subsurface pressures of 0.25-10,000 bar, and a wide range of concentrations of reactants). The free energy of reactions falls short by anywhere from 10 to 400 kJ/mol (for details see SI: Potential pathways for phosphine production; Figure S9). In particular, we quantitatively rule out the hydrolysis of geological or meteoritic phosphide or disproportionation of atmospheric phosphorous acid as the source of Venusian phosphine.

The lifetime of phosphine on Venus is key for understanding production rates that would lead to accumulation of few-ppb concentrations. This lifetime will be much longer than on Earth, whose atmosphere contains substantial molecular oxygen and its photochemically-generated radicals. The lifetime above 80 km on Venus (in the mesosphere²²) is consistently predicted by models to be $<10^3$ seconds, primarily due to high concentrations of radicals that react with, and destroy, PH_3 . Near the atmosphere's base, estimated lifetime is $\sim 10^8$ seconds due to thermal-decomposition (collisional-destruction) mechanisms. Lifetimes are very poorly constrained at intermediate altitudes (<80 km), being dependent on abundances of trace radical species, especially chlorine. These lifetimes are uncertain by orders-of-magnitude, but are substantially longer than the time for PH_3 to be mixed from the surface to 80 km ($< 10^3$ years). The lifetime of phosphine in the atmosphere is thus no longer than 10^3 years, either because it is destroyed more quickly or because it is transported to a region where it is rapidly destroyed. The SI (including Figs S7-12; Tables S2-3) details our methods.

We estimate the out-gassing flux of PH_3 needed to maintain ~ 10 ppb levels, taking the column of phosphine derived from observations and dividing this by the chemical lifetime of phosphine in Venus' atmosphere (Figure 5). The total outgassing-flux necessary to explain ~ 10 ppb of PH_3 is $\sim 10^6$ - 10^7 molecules $\text{cm}^{-2} \text{s}^{-1}$ (shorter lifetimes would lead to higher flux requirements). Photochemically-driven reactions in Venus' atmosphere cannot produce phosphine at this rate. To generate PH_3 from oxidized P-species, photochemically-generated radicals have to reduce the phosphorus by abstracting oxygen and adding hydrogen – requiring reactions predominantly with H, but also with O and OH radicals. Hydrogen-radicals are rare in Venus' atmosphere because of low concentrations of potential hydrogen-sources (species such as H_2O , H_2S that are UV-photolyzed to produce H radicals). We model a network of forward-reactions (i.e. from oxidized P-species to PH_3), not only as a conservative maximum-possible production rate for PH_3 , but also because many of the back-reaction rates are not known. We find the reaction rates of H radicals with oxidized phosphorus species are too slow by factors of 10^4 - 10^6 under the temperatures and concentrations in the Venusian atmosphere (Figure 5).

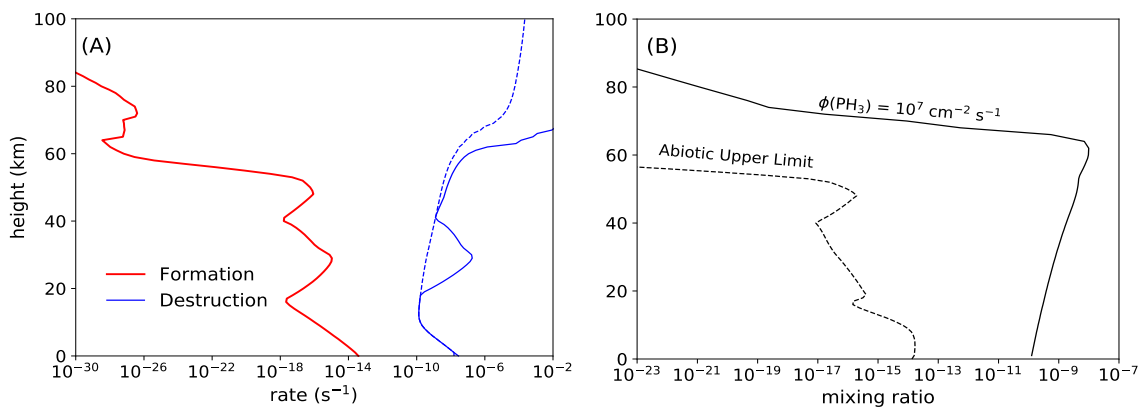


Fig. 5. Predicted maximum photochemical production of PH_3 (see kinetic network of Fig. S9), found to be insufficient to explain observations by more than four orders of magnitude. Left panel, (A): Upper limits of the predicted photochemical production rates (excluding transport) (red curve, s^{-1}) compared to photochemical destruction rates (blue curve, s^{-1}), including radicals and atoms (blue solid) and ignoring radicals and atoms (blue dashed), as a function of height (km). Right panel, (B): Mixing ratio of PH_3 as a function of atmospheric height (km), for a production flux within the cloud layer (~ 55 - 65 km) of $10^7 \text{ cm}^{-2} \text{ s}^{-1}$ (solid curve), compared to the predicted steady state abiotic upper limit (dashed curve).

Energetic events are also not an effective route to making phosphine. Lightning may occur on Venus, but at sub-Earth activity levels³³. We find that PH₃-production by Venusian lightning would fall short of few-ppb abundance by factors of 10⁷ or more. Similarly, there would need to be > 200 times as much volcanic activity on Venus as on Earth to inject enough phosphine into the atmosphere (up to ~10⁸, depending on assumptions about mantle rock chemistry). Orbiter topographical studies suggest there are not many large, active, volcanic hotspots on Venus³⁴. Meteoritic delivery adds at most a few tonnes of phosphorus per year (for Earth-like accretion of meteorites). Exotic processes like large-scale tribochemical (frictional) processes and solar wind protons also only generate PH₃ in negligible quantities (see SI: Potential pathways for phosphine production; Table S4; ref. 35).

Discussion

If no known chemical process can explain PH₃ within the upper-atmosphere of Venus, then it must be produced by a process not previously considered plausible for Venusian conditions. This could be unknown photochemistry or geochemistry, or possibly life. Information is lacking – as an example, the photochemistry of Venusian cloud droplets is almost completely unknown. Hence a possible droplet-phase photochemical source for PH₃ must be considered (even though phosphine is oxidised by sulphuric acid). Questions of why hypothetical organisms on Venus might make phosphine are also highly speculative (see SI: PH₃ and hypotheses on Venusian life).

Quantitatively, we can note that the production rates of ~10⁶-10⁷ molecules cm⁻² s⁻¹ inferred above are lower than the production by some terrestrial ecologies, which make the gas¹⁰ at 10⁷-10⁸ PH₃ cm⁻² s⁻¹. Considering also distribution, the phosphine on Venus is at or near temperate altitudes, and is also lacking around the polar caps. It is suggested³⁶ that the mid-latitude Hadley circulation cells offer the most stable environment for life, with circulation times of 70-90 days being adequate for reproduction of (Earth-analog) microbes. Phosphine is not detected by ALMA above an ~60° latitude-bound, agreeing within ~10° with the proposed upper Hadley-cell boundary³⁷ where gas circulates to lower altitudes. However, further work on diffusion processes is desirable (see SI: horizontal transport; Fig. S12).

In the context of Solar-System biosignature searches, our observations of the PH₃ 1-0 line have proved powerful for modest facility time (<10 hours on-source). The phosphine abundance is well-enough constrained (within factors ~2-3) for worthwhile modelling, and no *ad-hoc* introduction of temporal effects is needed. We have ruled out contaminants, and narrow lines mean that a presently-unknown chemical species would need to have a transition at an extremely nearby wavelength to mimic the PH₃ 1-0 line. However, confirmation is always important for a single-transition detection. Other PH₃ transitions should be sought, although observing higher-frequency spectral features may require a future large air- or space-borne telescope.

Even if confirmed, we emphasize that the detection of phosphine is not robust evidence for life, only for anomalous and unexplained chemistry. There are substantial conceptual problems for the idea of life in Venus' clouds – the environment is extremely dehydrating as well as hyper-acidic. However, we have ruled out many chemical routes to phosphine, with the most-likely ones falling short by 4-8 orders of magnitude (Table S4). To further discriminate between unknown photochemical and/or geological processes as the source of Venusian phosphine, or to determine if there is life in the clouds of Venus, substantial modelling and experimentation will be important. Ultimately, a solution could come from revisiting Venus for *in situ* measurements or aerosol return.

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Data and materials availability: The raw data from JCMT and ALMA are publicly available at websites <https://www.eaobservatory.org/jcmt/science/archive/> and <http://almascience.eso.org/aq/>. Our reduction scripts that can be used to reproduce the results shown are attached, as files Data S1 (JCMT) and Data S2-S4 (ALMA).

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