No evidence of phosphine in the atmosphere of Venus from independent analyses

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The detection of phosphine (PH3) in the atmosphere of Venus has been recently reported on the basis of millimetre-wave radio observations1 and their reanalyses2–5. In this Matters Arising we perform an independent reanalysis, identifying several issues in the interpretation of the spectroscopic data. As a result, we determine sensitive upper limits for PH3 in Venus’s atmosphere (>75 km, above the cloud decks) that are discrepant with the findings in refs. 1–3.

The measurements target the fundamental first rotational transition of PH3 (J = 1–0) at 266.944513 GHz, which was observed with the James Clerk Maxwell Telescope (JCMT) in June 2017 and with the Atacama Large Millimeter/submillimeter Array (ALMA) in March 2019. This line’s centre is near the SO2 (J = 30_21–31_22) transition at 266.943329 GHz (only 1.3 km s−1 away from the PH3 line), which represents a potential source of contamination. The JCMT and ALMA data, as presented in ref. 1, are at spectral resolutions comparable to the frequency separation of the two lines. Moreover, the spectral features identified are several kilometres per second in width, and therefore do not permit distinct spectroscopic separation of the candidate spectral lines of PH3 and SO2. We present the radiative transfer modelling we have performed and then discuss the ALMA and JCMT analyses in turn.

ALMA reanalysis

The analysis of interferometric data is relatively complex, in particular for bright and extended sources such as Venus (15.2 arcsec angular diameter for the ALMA data). The completeness of the different baselines (short and long) determines the ability to accurately measure the total planetary flux density1, while the bandpass calibration is a crucial factor in the ultimate quality of the resulting spectra12. The details of the calibration and imaging used during data reduction can have a dramatic impact on the quality and validity of the resulting ALMA interferometric data. The extracted spectra in extended data fig. 4 and the interferometric map in extended data fig. 3 of ref. 1 show large quasiperiodic fluctuations in the spectrum, which in ref. 1 is fitted with high-order polynomials. Particularly challenging is the fact that these fluctuations have a pattern/width comparable to their defined PH3 line core region. As we present in Supplementary Section 2 and as also reported in refs. 12, artificially produced features that mimic true atmospheric lines can be produced when analysing data with such characteristics.

Many of these large fluctuations can be introduced by the particular parameters used in calibration during data reduction. After the publication of ref. 1 we notified the North American ALMA Science Center team of substantial differences in the final spectra when applying different treatments of the bandpass calibrations—specifically, the type of bandpass calibration solution (traditional channel to channel versus polynomial fitted versus smoothed), and in particular enabling the ‘usescratch=True’ setting in Common Astronomy Software Applications (CASA)’s setjy for the model used for Callisto (the bandpass calibrator). The newly reprocessed data from the Joint ALMA Office (JAO) take these issues into consideration and are used by refs. 24. We analysed the data as presented originally in ref. 1 and could not recover a PH3 signature (Fig. 1b) and, we also reduced the ALMA data using the new JAO scripts as the starting point. We employed three separate procedures by three different groups (National Aeronautics and Space Administration Goddard Space Flight Center—NASA/GSFC, Berkeley, and National Radio Astronomy Observatory—NRAO), making use of different methods to evaluate the significance of the reported ALMA PH3 signatures. The three methods are the following: (1) employing the updated JAO scripts throughout (using CASA only, done at NASA/GSFC); (2) employing the updated JAO scripts, but proceeding independently beyond self-calibration (using CASA only; done at Berkeley)—note that phase-only self-calibration was done but not amplitude self-calibration, because the latter can be problematic for extended sources1; (3) as (2), but with the post-JAO-script reduction done in the Astronomical Image Processing System (AIPS).
(using both CASA and AIPS, done at NRAO). We investigated including/removing certain baselines; further details of the methods can be found in Methods and in Supplementary Section 2. All these analyses used the common foundation of the revised JAO scripts to carry out the initial calibration (in particular the bandpass and complex gain versus time calibrations), and very similar steps in the further data reduction (phase-only self-calibration, continuum subtraction, forming the image cube and extracting the disk-averaged spectrum).

The quality of the bandpass calibration was improved with the updated JAO scripts, yet the residual spectrum still showed notable large fluctuations (we found that a sixth-order polynomial captured most of the residual large fluctuations for method 1; ref. 1 considered a 12th order). Our other two reanalyses (2 and 3) led to practically flat spectra only needing second-order polynomial baselines (more information on the origin of these differences is explained in Supplementary Section 2). Ultimately, all our analyses of the data using these different approaches and methodologies reveal no conclusive signature of PH3 (Fig. 1), leading to an upper limit of \(<1\) part per billion by volume (ppbv) (3σ when employing a linewidth of \(0.186\) cm\(^{-1}\) atm\(^{-1}\)). When employing other proposed linewidths, the upper limit would be \(\text{PH}_3 < 0.7\) ppbv (linewidth of \(0.12\) cm\(^{-1}\) atm\(^{-1}\)) or \(<1.5\) ppbv (linewidth of \(0.286\) cm\(^{-1}\) atm\(^{-1}\)). This upper limit is also consistent with other recently reported upper limits derived from infrared ground-based observations (\(\text{PH}_3 < 5\) ppbv)\(^9\) and from spacecraft data (\(\text{PH}_3 < 0.2\) ppbv)\(^10\). We further validated our analysis of the ALMA data by analysing other SO\(_2\) and HDO lines in the same dataset (Supplementary Section 3).
The analysis of JCMT spectral data in ref. 1 involved fitting of multiple polynomials for the purpose of continuum subtraction: an initial fourth-order polynomial was removed, then a ninth-order polynomial was removed from a smoothed spectrum and finally a masked eighth-order polynomial was removed. Recently, Thompson explored the robustness of the two detection methods used in ref. 1, namely low-order polynomial fits and higher-order multiple polynomial fits, and found that neither line detection method is able to recover a statistically significant detection at the position of the PH$_3$/SO$_2$ line.

We investigate whether a weak PH$_3$ signature, if present, could be distinguished from SO$_2$ contamination, and what its contribution to the detected signal could be. To explore this, we employed the same VIRA45 temperature–pressure (T–P) profile as used by Greaves et al. (their extended data fig. 8) and the SO$_2$ profile presented in their extended data fig. 9 (~100 ppbv in the 70–90 km region, dropping to <30 ppbv above 95 km). If this potential SO$_2$ contaminant signature were removed from the JCMT data, then the original feature would be confined within the noise (Fig. 2). We next modelled a mesospheric SO$_2$ profile as measured by Venus Express using solar occultation, and similar to case D of ref. 12 (SO$_2$ abundance of ~30 ppbv at 80 km, increasing to ~100 ppbv at 90 km and reaching ~300 ppbv at 95 km). Right: ‘Residual’ is obtained by removing the SO$_2$ signature from the JCMT data as modelled with a 3 km s$^{-1}$ resolution using the ref. 1 fig. 9 SO$_2$ profile. The ‘PH$_3$ Greaves + 2020’ spectrum is a model spectrum employing the PH$_3$ profile in ref. 1 fig. 9 (peaking at 60 km with 20 ppbv) and the default linewidth (0.186 cm$^{-1}$ atm$^{-1}$), while a model considering a vertically constant mixing ratio of 20 ppbv is labelled ‘PH$_3$ 20 ppbv constant’. ‘PH$_3$ Greaves + 2020’ is flat and featureless because these measurements only sample PH$_3$ above 75 km (Supplementary Section 4).

**Fig. 2 | Residual JCMT data and models of SO$_2$ and PH$_3$.** Left: JCMT data for their mid-range solution with masking within ±5 km s$^{-1}$, while ‘SO$_2$ Greaves + 2020’ is a model spectrum synthesized using the T–P in ref. 1 fig. 8 and the SO$_2$ profile in ref. 1 fig. 9. ‘SO$_2$ Belyaev + 2012’ is a typical profile in ref. 1 (fig. 9) and similar to ref. 12 (case D), with an SO$_2$ abundance of ~30 ppbv at 80 km, increasing to ~100 ppbv at 90 km and reaching ~300 ppbv at 95 km. Right: ‘Residual’ is obtained by removing the SO$_2$ signature from the JCMT data as modelled with a 3 km s$^{-1}$ resolution using the ref. 1 fig. 9 SO$_2$ profile. The ‘PH$_3$ Greaves + 2020’ spectrum is a model spectrum employing the PH$_3$ profile in ref. 1 fig. 9 (peaking at 60 km with 20 ppbv) and the default linewidth (0.186 cm$^{-1}$ atm$^{-1}$), while a model considering a vertically constant mixing ratio of 20 ppbv is labelled ‘PH$_3$ 20 ppbv constant’. ‘PH$_3$ Greaves + 2020’ is flat and featureless because these measurements only sample PH$_3$ above 75 km (Supplementary Section 4).

**JCMT analysis and SO$_2$ contamination**

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We next modelled a mesospheric SO$_2$ profile as measured by Venus Express using solar occultation, and similar to case D of ref. 12 (SO$_2$ abundance of ~30 ppbv at 80 km, increasing to ~100 ppbv at 90 km and reaching ~300 ppbv at 95 km). In this case, the SO$_2$ contamination signature is even stronger and fully captures the claimed PH$_3$ residual in refs. 1–3 (Fig. 2). A comprehensive compilation of SO$_2$ measurements, including thousands of measurements from the Venus Express orbiter at ultraviolet and infrared wavelengths as well as ground-based observations, show that SO$_2$ abundances at 80 km are frequently well in excess of 100 ppbv, with peak abundances occasionally exceeding 1,000 ppbv. This shows that the SO$_2$ profiles we adopted are well within usual ranges of variability observed on Venus (more information about the considered profiles can be found in Supplementary Section 1). Having shown that the absorption line can be reproduced by a reasonable vertical profile of SO$_2$, we therefore argue that this absorption line cannot be definitively attributed to PH$_3$.

**Probing altitude**

We also explored the altitudes from which these absorptions originate, which can be used to constrain photochemical models and facilitate comparison with other measurements. This is ultimately related to the spectroscopic parameters of the targeted line and of the competing radiative active species in this spectral region. When considering the linewidth of 0.186 cm$^{-1}$ atm$^{-1}$ for PH$_3$ at 70 km (3.4 × 10$^{-2}$ atm) the line would be 213 km s$^{-1}$ wide, that is, much broader than the narrow window region of ±5 km s$^{-1}$ or ±10 km s$^{-1}$ searched for PH$_3$. As a polynomial is fitted and subtracted, removing any spectral line information beyond this core region, the spectral information at broader widths (originating from lower altitudes) is thus removed. Our models predict an observable PH$_3$ absorption at this frequency only when PH$_3$ is present above 75 km (see details in Supplementary Section 4), and therefore these data provide no constraints on its abundance in the cloud deck (50–70 km), in contrast to refs. 1–3. This can be seen in Fig. 2: a flat spectrum is calculated for the PH$_3$ profile determined from the chemical modelling described in ref. 1, in which PH$_3$ is present only below 70 km altitude.

**Conclusions**

By our independent analysis of the ALMA data, we set a limit of 1 ppbv for PH$_3$. We also show that the observed JCMT feature could be attributed to mesospheric SO$_2$ gas. Furthermore, for any PH$_3$ signature to be recoverable in either ALMA or JCMT analyses, PH$_3$ needs to be present at altitudes above 75 km. We conclude that the recent identification of PH$_3$ in the upper atmosphere of Venus is not supported.
Methods
We have employed three independent radiative transfer models: the Planetary Spectrum Generator (PSG; https://psg.gsfc.nasa.gov)\(^2\), the Non-linear Optimal Estimator for Multivariate Spectral Analysis (NEMESIS; https://nemesiscode.github.io)\(^3\), and the Center for Astrophysics planetary modelling tool\(^4\). The Planetary Spectrum Generator radiative transfer analysis included the latest HITRAN SO\(_2\) line parameters for a CO\(_2\) atmosphere\(^5\), a layer-by-layer, line-by-line study, and a full disk sampling scheme with 10 concentric rings. The NEMESIS analysis was also performed in line-by-line mode, and used the same spectroscopic data with a five-point Gauss-Lobatto disk integration scheme. As described in ref. 1, there is some uncertainty in the line-shape parameters for the PH\(_3\) line in a CO\(_2\) atmosphere. HITRAN reports an air linewidth of 0.067 cm\(^{−1}\), which would correspond to 0.12 cm\(^{−1}\) in a CO\(_2\) atmosphere if the value were scaled by the typical 1.8 scaling ratio observed for the SO\(_2\) lines\(^6\). Greaves et al. considered a theoretical estimate of 0.186 cm\(^{−1}\), and an upper range of 0.286 cm\(^{−1}\) measured for the NH\(_3\) line in a SO\(_2\) atmosphere. Considering the uncertainty on this parameter, we adopt the same value as Greaves et al.\(^6\) by default (0.186 cm\(^{−1}\)).

When reducing the ALMA data, we downloaded the raw data and scripts as provided in the archive. By three separate reduction methods, we then used the provided scripts along with well established techniques in the calibration and imaging of radio interferometric data to obtain final disk-averaged spectra for Venus. There are three scripts provided with the data: (1) a calibration script; (2) an imaging preparation script; (3) an imaging script. The calibration script calculates and applies several system calibrations and flags data known to be invalid, then sets the model for Callisto and uses this for flux density scale and bandpass calibration (using a third-order polynomial fit to the bandpass amplitude), then carries out a complex gain versus time calibration using the calibrator J2000-1748. The imaging preparation script Doppler shifts the spectral axis of the various spectral windows, then images Venus and uses that image to carry out phase-only self-calibration, then sets the model for Venus and carries out amplitude self-calibration.

The imaging script then makes a continuum image, carries out continuum subtraction and makes the image cube. In both the continuum image and the image cube a primary beam correction is made, since the primary beam at these frequencies (with a full-width at half-maximum of ~24°) resolves the disk of Venus (diameter ~15.2°) at these wavelengths. There is some uncertainty in the line-shape parameters for the PH\(_3\) line in a CO\(_2\) atmosphere. HITRAN reports an air linewidth of 0.067 cm\(^{−1}\), which would correspond to 0.12 cm\(^{−1}\) in a CO\(_2\) atmosphere if the value were scaled by the typical 1.8 scaling ratio observed for the SO\(_2\) lines\(^6\). Greaves et al. considered a theoretical estimate of 0.186 cm\(^{−1}\), and an upper range of 0.286 cm\(^{−1}\) measured for the NH\(_3\) line in a SO\(_2\) atmosphere. Considering the uncertainty on this parameter, we adopt the same value as Greaves et al.\(^6\) by default (0.186 cm\(^{−1}\)).

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**Author contributions**

G.L.V., P.G.J.I., M.G., V.K. and G.L. performed the retrievals and the radiative-transfer modelling. M.C., I.d.P. and B.B. calibrated and analysed the ALMA data. S.N.M., C.A.N., R.C., A.E.T., A.M., S.C., N.B. and K.R.d.K. assisted with the interpretation of the interferometric spectra. C.F.W., S.F., T.J.F., M.L., P.H., G.N.A., A.M.M., A.C.V. and R.K. assisted with the interpretation of the results in the context of the Venusian atmosphere and its photochemistry. All authors contributed to writing and revising the manuscript.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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