AMENDMENTS
https://doi.org/10.1038/s41550-021-01423-y

nature astronomy

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Addendum: Phosphine gas in the cloud deck of Venus

Jane S. Greaves, Anita M. S. Richards, William Bains, Paul B. Rimmer, Hideo Sagawa, David L. Clements, Sara Seager, Janusz J. Petkowski, Clara Sousa-Silva, Sukrit Ranjan, Emily Drabek-Maunder, Helen J. Fraser, Annabel Cartwright, Ingo Mueller-Wodarg, Zhuchang Zhan, Per Friberg, Iain Coulson, E'lisa Lee and Jim Hoge

Addendum to: *Nature Astronomy* https://doi.org/10.1038/s41550-020-1174-4, published online 14 September 2020.

In our Article, we published spectra of phosphine molecules in Venus's clouds, following open-science principles in releasing data and scripts. In the process, it was found that the standard Atacama Large Millimeter/submillimeter Array (ALMA) calibration procedures are unsuitable for such an exceptionally bright target. The Joint ALMA Observatory then issued a revised calibration. We have replied to most of these issues in a separate publication[1]. Some misconceptions about detrending of spectral baselines also emerged. Here we present evidence, using further detailed analysis mainly of the James Clerk Maxwell Telescope (JCMT) PH_3 discovery data, that detrending was done correctly. Firstly, we show that mathematically correct polynomial fitting of periodic ripples does not lead to 'fake lines' (probability <~1.5% for JCMT). Secondly, we show that such ripples can be characterized in a non-subjective manner via Fourier transforms (FTs). A 20 ppb PH_3 feature is ~5 standard deviations (σ) compared to the JCMT baseline uncertainty, and is distinctive as a narrow perturber of the periodic ripple pattern. Thirdly, the structure of the FT-derived baseline demonstrates that polynomial fitting, if unguided, can amplify artefacts and so artificially reduce the significance of real lines.

Our discovery of phosphine in Venus's clouds has sparked much debate—unexpected in an oxidized atmosphere, it suggests a novel chemical origin[2], or even a contribution of life in a hyperacidic aerial biosphere[3]. Other work has provided PH_3 limits[4,5] and detections[6] at lower and higher altitudes. Our Article described the detection of the $J = 1–0$ rotational transition of PH_3 using both JCMT and ALMA data to provide a robustness check, other transitions being very difficult to access with existing telescopes. Recent re-interpretations[7–9], after adapting and re-running our published scripts, have suggested that the JCMT and/or ALMA data do not demonstrate detection of the PH_3 $J = 1–0$ line, even though we demonstrated that using polynomial-trendline fitting did not make PH_3 lines 'appear', and used a 'double-coincidence' test (without polynomial fitting) to show that only the PH_3 line was common to both datasets. Some of the misunderstandings of detrending in heterodyne spectroscopy are further clarified here.

Testing for fake lines

We verify that the phosphine line is unlikely to be an artefact generated by polynomial fitting. To be clear, we do not dispute that polynomial fitting can identify instrumental features similar to absorption lines, and indeed amplify them under some constraint violations (see Supplementary Information). However, hypothesis testing should not be confused with hypothesis generation—essentially assuming that the PH_3 identification was a post hoc rationalization of a feature found after complex processing. In fact, Venusian PH_3 was a prior hypothesis (see abstract number 2018.A.00023.S (Cycle 6 DDTs) at https://almascience.eso.org/observing/highest-priority-projects) that we tested with data. Specifically, the line's passband position was predicted, and so any 'fake lines' had to not only show absorption but also show absorption at a pre-specified location. We re-examine this here, using the JCMT data, with the ALMA data now being essentially free of ripples[1] (see Supplementary Information).

In our Article, we employed three tests: (1) a planetary absorption line should lie where expected from the transition's rest frequency and the Doppler shift, (2) the line width should be appropriate to the atmospheric physics, and (3) the amplitude should be negative relative to the continuum. These tests are not all likely to be met by a random ripple, although the probability does increase if there are many ripples in the passband.

Here (1) was the most important criterion, with (2) less rigorous (as the PH_3-CO_2 collisional line-broadening coefficient is unmeasured). We now re-test (1) by examining how many 'draws' are needed to yield a feature coincident with pre-specified locations in the JCMT spectrum. Random test frequencies can be used, but we included rest frequencies of molecules that are improbable in Venus's clouds (see Supplementary Information). This can additionally show whether potential mis-identifications could occur, for example, where only one of a family of lines of a molecule is seen.

Figure 1 shows that very few draws produced 'absorptions' that agreed with the predicted location. There are only three candidates, with two close to the largest instrumental ripples in the passband (while PH_3 $J = 1–0$ is not in such a location), and the third an unconvincing fit (50% uncertainty in derived width). We thus estimate that the chance of any instrumental feature passing our tests and not being readily recognized as an artefact is under ~1.5% (<1 among 72 draws). The probability may be lower, but no further independent tests are possible within the limited bandpass (see Supplementary Information).

Thompson[9] performed JCMT draws using the same scripts, and concluded that 25% of them could produce a feature of larger amplitude than the PH_3 line. Here we find ~12% of draws are in absorption and deeper than PH_3, but only ~3% (2/72) have as good positional agreement and velocity uncertainty as the real PH_3 line, and these are identifiably instrumental (Fig. 1).

Fourier analysis of baselines

We also performed, using JCMT data, additional tests to verify that a 'low-σ' feature (following the definition proposed by Snellen et al.[7]) can be a significant outlier among non-random periodic ripples.

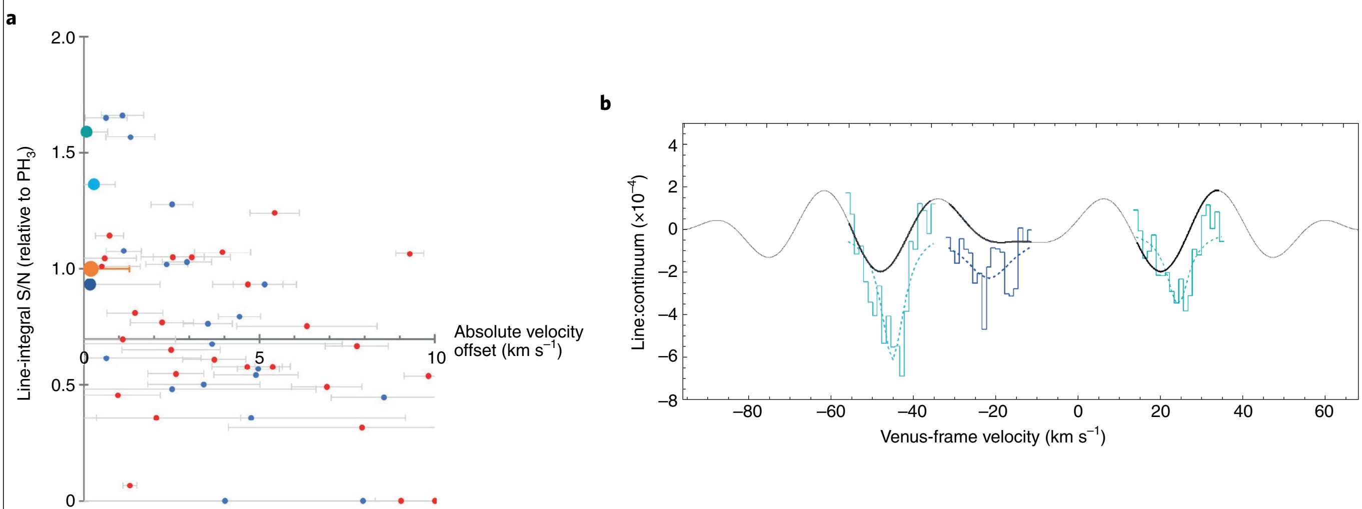

Fig. 1 | Assessing the probability of a 'fake line' detection in the JCMT data. a, Line-integrated signal-to-noise ratio (S/N) (relative to PH_3, set to 1) plotted against offset of the line centre from velocity expected in the Venus reference frame, with 1σ error bars from the automated fits. Red and blue symbols are respectively for the draws giving a positive ('emission') or negative ('absorption') result. The orange point shows PH_3 $J = 1$–0 (S/N = 4.3, line integrated; the axis intercept marks S/N = 3). Lines were automatically characterized using Lorentzian fits in a line-centred window. Only the three points shown with larger symbols agree within errors with the expected velocity and are in absorption with S/N > 3. **b**, For these three extracted features, the central parts of the spectra (histograms) and their Lorentzian fits (dashed) are plotted over the net baseline (black curve) defined by Fourier components. Thicker black sections highlight where two features (turquoise, light blue) are close to the largest ripples; the third feature (dark blue) is poorly defined (uncertainty of ±50% in width). The turquoise, light blue and dark blue features have correspondingly coloured points in **a** (the larger symbols from top-to-bottom).

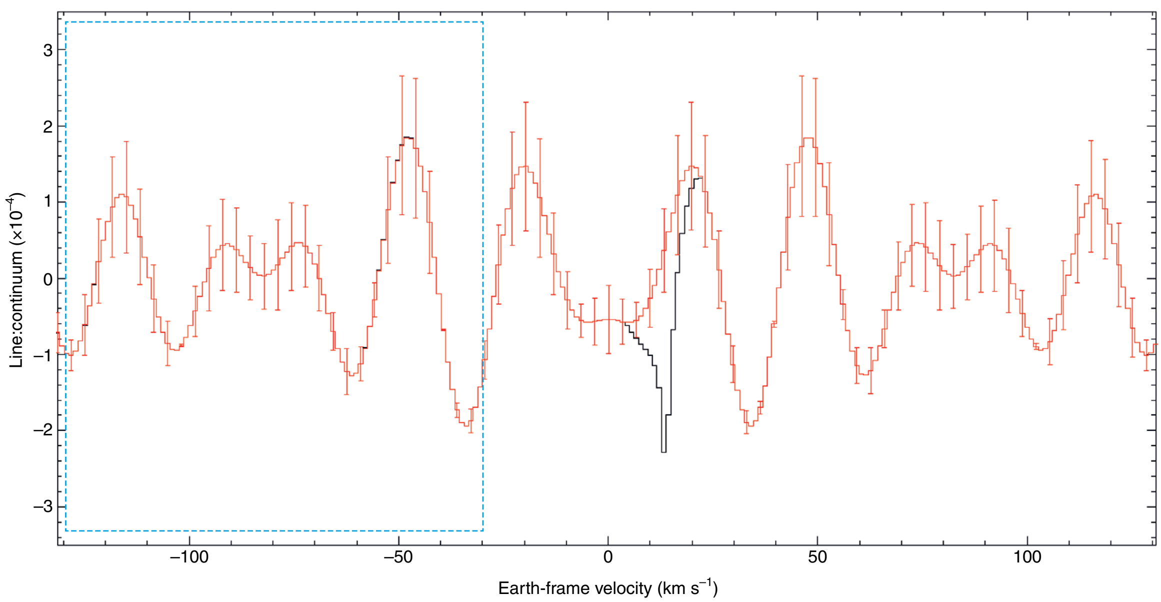

Fig. 2 | Analysing the detectability of a real line in the JCMT data. Fourier-component model for the net JCMT baseline (in red), with 20 ppb PH_3 model added (in black). The PH_3 radiative-transfer model was shifted to the instrumental velocity frame and median filtered over 35 km s^{-1} intervals, as in our original work. Red bars show the standard errors derived from the dispersion among the model baselines of different observations. The line-minimum signal is -2.65×10^{-4} and the baseline uncertainty in this spectral channel is 0.55×10^{-4}. The dashed blue box indicates an example of a window in the passband that has a low number of distinguishable ripples: the three bumps around −70 to −90 km s^{-1} merge into one feature of the same signal level within the uncertainties.

As described in the Supplementary Information, FT components can be identified in the frequency–time plane of the JCMT dataset. We identify six major components, >10σ above the FT noise. These arise from four different ripple periods and two periodicities over time. An inverse FT of these components then generates a set of spectral baselines, with no subjective intervention.

In Fig. 2, we show the net baseline from this procedure, along with the dispersions that result because the ripples are not the same in each observation. The superposed PH_3 model (20 ppb) is then a clear outlier—it perturbs the periodicity of the ripples, and is narrower than the ripple 'bumps'.

Here, the line minimum would be only 3σ by the definition of Snellen et al.[7], that is, comparing it to the standard deviation of the ripple pattern. However, it is 4.8σ compared to uncertainty in the spectral baseline, allowing for a significant detection if the measurement noise is sufficiently small.

There are some sections of model baseline (Fig. 2) where the ripples are not distinguishable above the noise, for example around $\pm$70–90 km s^{-1}. This can explain the results of Thompson[9] where some polynomial fits yielded features of higher amplitude than the PH_3 line. The constant order provided in our scripts (8th, optimized for the PH_3 line region) will allow too much freedom in a section of passband with few distinguishable bumps. In such cases, artificially amplified features can easily occur.

This Fourier analysis intentionally uses minimal intervention, and is intended only to demonstrate an approach that is non-subjective. In reality, the ripple artefacts changed between observations, in the number of periods seen and in their amplitudes and phases, so line extraction needs to be done per observation. The number of $>5\sigma$ FT components in individual observations is 2–8 (that is, the 9 constants of the original polynomial fits were needed in at least some cases). Further-developed FT solutions, to be presented in future work, may be able to both remove subjectivity and flatten the entire passband.

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Acknowledgements

S. Mairs and M. J. Currie also contributed to this Addendum.

Additional information

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41550-021-01423-y.

Published online: 16 July 2021

https://doi.org/10.1038/s41550-021-01423-y