Is Phosphine in the Mass Spectra from Venus’ Clouds?

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Considering the implications of the reported single spectral line detection of phosphine (PH$_3$) by Greaves et al.$^1$, we were inspired to re-examine data obtained from the Pioneer-Venus Large Probe Neutral Mass Spectrometer (LNMS)$^{2-5}$ to search for evidence of phosphorus compounds. The LNMS obtained masses of neutral gases (and their fragments) at different altitudes within Venus’ clouds. Published mass spectral data$^2$ correspond to gases at altitudes of 50-60 km, or within the lower and middle clouds of Venus – which has been identified as a potential habitable zone$^6-10$. We find that LMNS data support the presence of phosphine; although, the origins of phosphine remain unknown.

As shown in Figure 1, we focused on low-mass species in the range of 15-40 atomic mass units (amu). To estimate the resolution and resolving power of the LNMS, we first compared measured and expected$^{11}$ masses for CO$_2$, SO$_2$, N$_2$, $^{40}$Ar, and $^{36}$Ar, which were identified by Hoffman et al.$^{2-4}$. In all cases, measured masses (from the spectra) and expected masses differed by <0.003 amu. As noted by Hoffman and colleagues, the “high-resolution” data allowed for sufficient separation and identification of species including $^{40}$Ar (39.965 amu; measured) and C$_3$H$_4$ (40.029 amu; measured) – due to reasonable confidence in the 3$^{rd}$ and 4$^{th}$ significant digits in the amu values. Additionally, sensitivities were stated as “1 part per million (ppm)”$^3$, upper counting rates (or intensities) in the data$^2$ were $\sim 1.8 \times 10^6$ (e.g., CO$_2$), and identities were assigned to mass values with counting rates as low as 9 (e.g., $^{37}$Cl)$^{2,3}$. Moreover, as per our understanding, several chemical identities (“lookup nouns”) were essentially pre-determined (e.g., sulfur, oxygen, O$_2$, H$_2$S, SO$_2$, and CH$_4$) and used to permit microprocessor selection of the mass ranges analyzed during descent.$^4$

In this light, we leveraged the high-resolution data and dynamic range to uncover the presence of phosphine. We note that phosphorous compounds were not reported in the initial analyses$^2$, and that phosphorous has only been detected in Venus’ clouds by the VeGa lander via X-ray diffraction$^{12}$. To assign chemical identities in the LNMS mass spectra, we assumed a conservative mass unit resolution of $\leq$0.006 amu, which was 2-fold higher than the noted accuracies. Counting rates for most species were between $10^1$-$10^5$ amu, or within the stated
range of sensitivity. For signals with similar masses, chemical identities were only assigned when the differences between the masses ($\Delta m$) was $\geq 0.010$ amu. For all comparative mass pairs, these constraints effectively corresponded to a resolving power range of ~700-2600 (resolving power = $m/\Delta m$), which is consistent with the reported value of $\geq 440$ (10% valley) for the LNMS.

Under these assumptions, we obtain the following tentative conclusions (Figure 1):

- **Mass spectra show evidence for atomic phosphorous (30.973 amu), sulfur (31.972 amu), and oxygen (15.995 amu), where all measured masses differ from expected masses by $\leq 0.001$ amu (P, 30.973907 amu; S, 31.972071 amu; O, 15.995000 amu). These data further confirm acquisition of high-resolution data by the LNMS.**

- **Mass spectra show the presence of PH$_3$ when considering the following:**
  - Atomic phosphorous and sulfur are unambiguously assigned.
  - The signal at 33.992 amu represents PH$_3$ (33.997382 amu), or a composite mass$^a$ containing roughly equal abundances of PH$_3$ (33.997382 amu) and H$_2$S (33.987721 amu). [Example calculation: 33.992 amu $\approx$ 33.9925516 amu = 50%*$33.99738$ amu PH$_3$ + 50%*$33.987721$ amu H$_2$S.]
  - The signal at 32.985 amu represents PH$_2$ (32.989557 amu), or a composite mass$^a$ containing roughly equal abundances of PH$_2$ (32.989557 amu) and HS (32.979896 amu), which is a fragment of H$_2$S. [Example calculation: 32.985 amu = 32.9847266 amu = 50%*$32.989557$ amu PH$_2$ + 50%*$32.979896$ amu HS.]
  - The fragment of PH (31.981732 amu) cannot be detected since it is (A) masked by O$_2$ (31.990 amu, measured; 31.990000 amu, expected) and (B) below the limit of detection, as inferred from the NIST reference spectrum for PH$_3$$^b$, where intensities for PH are $\sim$15% of the parent ion.
  - When considering deuterium$^c$, the signal at 35.005 amu is consistent with PH$_2$D as the dominant species, and is inconsistent with the presence of a composite mass including HDS. Any composite mass would fall between the expected mass values of 35.003659

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$^a$ For potential composite masses, we assume that LNMS had insufficient resolving power ($m/\Delta m > 3400$) to separate the mass pairs of PH$_2$ (32.989557 amu) and HS (32.979896 amu), and PH$_3$ (33.997382 amu) and H$_2$S (33.987721 amu).

$^b$ https://webbook.nist.gov/cgi/cbook.cgi?Name=phosphine&Units=SI

$^c$ For fragmented species, deuterium was not considered due to kinetic isotope effects, which may enrich hydrogen during the fragmentation reactions (Derrick. P.J., *Mass Spectrom. Rev.* 2 (1983)).
amu for PH$_2$D and 34.993998 amu for HDS. The signal of **35.005 amu** is outside this range, and is greater than the expected mass of PH$_2$D by ~0.001 amu. Further, the counting rate ratio of ~1.6 for PH$_3$/PH$_2$D is consistent with the equilibrium constant for conversion of PH$_2$D to PH$_3$ in liquid water (~1.6)$^{13}$.

- In the spectra (**Figure 1**), no other masses could be assigned to HDS – the signal at 34.972 amu was ill-matched due to a $\Delta$m=0.022 amu, and doubly charged HDS was not present.

- The signals at **34.972** and **36.966 amu** were consistent with $^{35}$Cl (34.968853 amu) and $^{37}$Cl (36.9659026 amu), which represents a refinement from prior assignments for $^{35}$Cl (from 35 amu)$^3$.

- When considered together, exclusion of a composite signal between PH$_2$D and HDS, and lack of detection of HDS, suggests an absence of H$_2$S, or that H$_2$S is much lower in abundance than PH$_3$. By extension, this supports assignment of **33.992** and **32.985 amu** as (predominantly) PH$_3$ and PH$_2$. Further, through re-assignment of chlorine isotopes, the signal at **35.005 amu** was available for interpretation as PH$_2$D.

- Lastly, the mass spectra show potential evidence of several other chemicals that are potentially incompatible with the oxidizing atmosphere of Venus:

  - Reported masses of **16.031**, **15.023**, and **17.026 amu** are consistent with CH$_4$ (16.031300), the CH$_3$ fragment (15.023475 amu), and CH$_3$D (17.037577 amu) or $^{13}$CH$_4$ (17.0346548 amu)$^2$.

  - Masses of **29.997** and **15.995 amu** are consistent with NO (29.998074 amu) and atomic oxygen (15.995000 amu); though multiple sources of oxygen are apparent from the counting rates.

  - Masses of **34.005** and **17.002 amu** are consistent with H$_2$O$_2$ (34.005650 amu) and the OH fragment (17.002825 amu).

To conclude, this re-evaluation of Venus’ mass spectra shows the detection of atomic phosphorous as a fragmentation product from a neutral gas. Moreover, the spectra show a tantalizing possibility for the presence of PH$_3$, along with its associated fragments, and singly deuterated parent ion. While intensities of the peaks are low, they are perhaps consistent with the ~20 ppb abundances$^1$ reported by Greaves et al. Together, the tentative assignments suggest that the reported abundances of H$_2$S (from mass spectra) across Venus’ atmosphere may actually be PH$_3$; and that atomic sulfur is derived from SO$_2$. These total interpretations also lend support to the presence of chemicals potentially out of equilibrium in Venus’ clouds (e.g., PH$_3$, O$_2$, CH$_4$, C$_3$H$_4$, NO, H$_2$, and H$_2$O$_2$). We believe this to be an indication of chemistries
not yet discovered, and/or chemistries potentially favorable for life. Looking ahead, and to better understand the potential for disequilibria in the clouds, we require a sustained approach for the exploration of Venus.

**Statement of Competing Interests**
The authors declare no competing interests.

**Statement of Author Contributions**
All authors (RM, SSL, MJW, & JAC) contributed to analytical discussions, assisted in preparation of the letter, approved of the submission, and agreed to be accountable for the respective contributions. RM is the corresponding author.

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Figure 1. Tentative assignments in the LNMS mass spectra. 

![Mass Spectra Diagram]

Color Scheme:
- blue = PH and fragments
- yellow = H₂S and fragments
- red = H₂ and fragments
- gray = NO and fragments
- purple = CH₄ and fragments
- orange = O₂
- clear = Cl isotopes
- green = potential mixture (PH₃ & H₂S)
- dark gray = potential mixture O₂ and PH₃