Some experimental data pro and contra the PH3 detection

Compiled by O. Korablev

Matters Arising *(Submitted to Nature, Matters Arising, 9/22/2020)*

Is Phosphine in the Mass Spectra from Venus' Clouds?

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amu	data
15.013	7680
15.018	16896
15.023	22528
15.028	22016
15.033	12800
15.995	335872
16.018	40960
16.031	39936
1.008	3520
17.002	296
17.026	244
17.985	336
18.010	1088
18.034	66
18.987	34
18.998	18
19.007	5
19.981	480
19.992	384
20.006	112
20.015	30
20.993	10
21.991	45056
21.995	47104
22.496	560
26.002	112
26.014	122
27.010	102
27.023	124
27.988	507904
27.995	606208
28.000	655360
28.005	671744
28.012	499712
28.032	122880
28.997	6656
29.003	7040
29.039	992
29.997	1024
30.046	208
30.973	11
31.006	26
31.972	128
31.990	320
2.016	22016
32.985	18
33.966	15
33.992	19
34.005	21
34.972	15
35.005	12
35.966	656
35.981	704
36.966	9
37.968	152
39.950	1376
39.958	1504
39.965	1664
39.972	1696
40.029	80

CH_3 (15.023475 amu)

(15.995000 amu) O

CH_4 (16.031300 amu)

(17.002825 amu) OH

mixture of $^{13}CH_4$ & CH_3D

(30.973907 amu) P

NO (29.998074 amu)

S (31.972071 amu)

(31.981732 amu) PH

O_2 (31.990 amu)

(32.989557 amu) PH_2

HS (32.979896 amu)

(33.997382 amu) PH_3

H_2S (33.987721 amu)

(34.005650 amu) H_2O_2

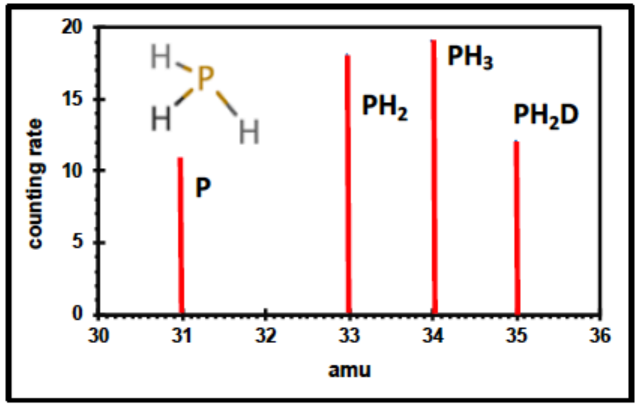
^{35}Cl (34.968853 amu)

(35.003659 amu) PH_2D

^{37}Cl (36.9659026 amu)

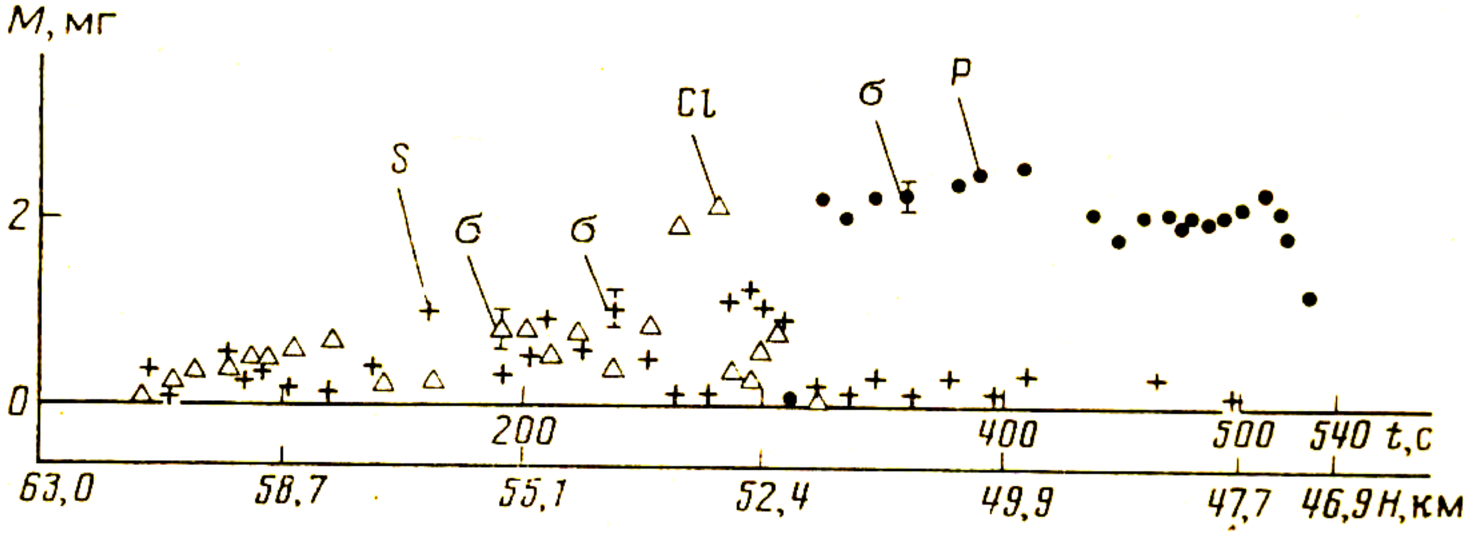
Color Scheme

- blue = PH_3 and fragments
- yellow = H_2S and fragments
- red = H_2O_2 and fragments
- gray = NO and fragments
- purple = CH_4 and fragments
- orange = O_2
- clear = Cl isotopes
- green = potential mixture (PH_x & H_xS)
- dark gray = potential mixture O_2 and PH)



From M. Gerasimov

Data of elemental analysis of cloud aerosols by instrument ИФП (IPhT Indicator of Phase Transitions) /VEGA which showed predominant phosphorus chemistry of low clouds. Phosphorus (black circles) concentration is dominant (to Cl and S) in the range of heights 47.0 — 52.3



Greaves et al. (2020) observed the line at 266.94451 GHz using JCMT and ALMA. They assign this line to a sum of SO_2 (10%), the remaining being PH_3. Abiotic sources of PH_3 are lacking on Venus, and this is claimed as an indication of life. Sandor et al. (2010) observed SO_2 on Venus for a few years using JCMT and the line at 346.65217 GHz. The observed quantity varied from 0 to 76 ppb and referred to altitudes above 85 km. The ALMA observations by Encrenaz et al. (2015) using the same line gave 12 ppb above 88 km.

Greaves et al. (2020, Fig. 4 left) observed the SO_2 line at 267.53745 GHz that shows SO_2 = 10 ppb. They do not specify the altitude that can be ~85 km based on the previous observations. This line is scaled to get ~10% of the observed PH_3 absorption in their Fig. 4 right.

Weighting function of the PH_3 line peaks at 56 km (supplementary Fig. 2), and "the weighting function shows the altitudes where the continuum (thermal) emission arises" (see the figure caption). Hence weighting function of the SO_2 contamination must peak at 56 km as well. However, the SO_2 abundance is ~10 ppm at 56 km (Krasnopolsky 1986, Photochemistry of the Atmospheres of Mars and Venus, Springer, p. 152). The model by Greaves et al. (2020, supplementary Fig. 9) shows a similar value, exceeding the 10 ppb in Fig. 4 by a factor of 1000. Therefore the line scaling in Fig. 4 looks doubtful, and the observed line can be completely SO_2 with no phosphine and life on Venus.

PH_3 can be searched on Venus using its strong lines at 4.1-4.4 mu. However, this rage refers to the altitudes above 68 km, where a strong depletion of PH_3 occurs by photolysis. More promising could be submillimeter observations using ALMA and PH_3 lines that are not contaminated by other species.
I have mailed two messages with my doubts to Dr. Greaves.

Vladimir A. Krasnopolsky

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https://doi.org/10.1038/s41550-020-1174-4

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Phosphine gas in the cloud decks of Venus

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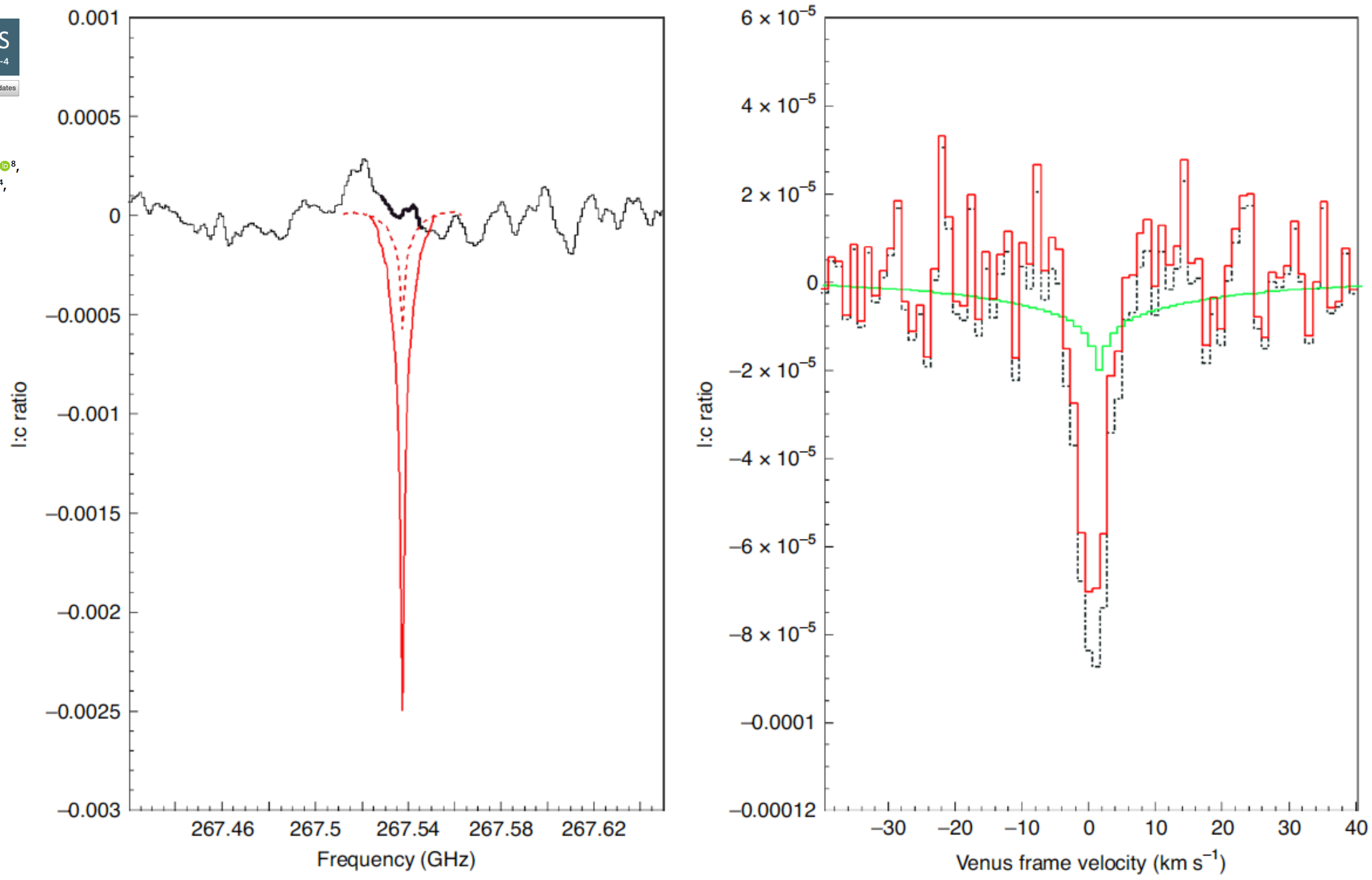

Fig. 4 | The process of estimating SO_2 contamination of the PH_3 line. Left: a section of ALMA wideband data (whole planet, after a third-order polynomial correcting for broad curvature has been removed), around the SO_2 $13_{3,11}$–$13_{2,12}$ rest frequency of 267.53745 GHz (wavelength ~1.121 mm). The thicker histogram over the ±10 km s^{-1} range illustrates that SO_2 absorption is not seen. The red dashed curve is an SO_2 10 ppb model, after subtracting a polynomial forcing line wings towards zero outside $|v| = \pm10$ km s^{-1}. 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 SO_2 line would need to have if the line we identify as PH_3 1–0 is instead all attributed to the SO_2 $30_{9,21}$–$31_{8,24}$ transition. Right: our model for the maximum allowed SO_2 $30_{9,21}$–$31_{8,24}$ contribution is re-plotted as a green histogram; this is, the red dashed model of the left panel, but without any polynomial subtraction. The PH_3 whole-planet spectrum of Fig. 2 (here a black dot-dashed histogram) is then re-plotted (red solid histogram) after subtraction of this maximized model of SO_2 $30_{9,21}$–$31_{8,24}$.

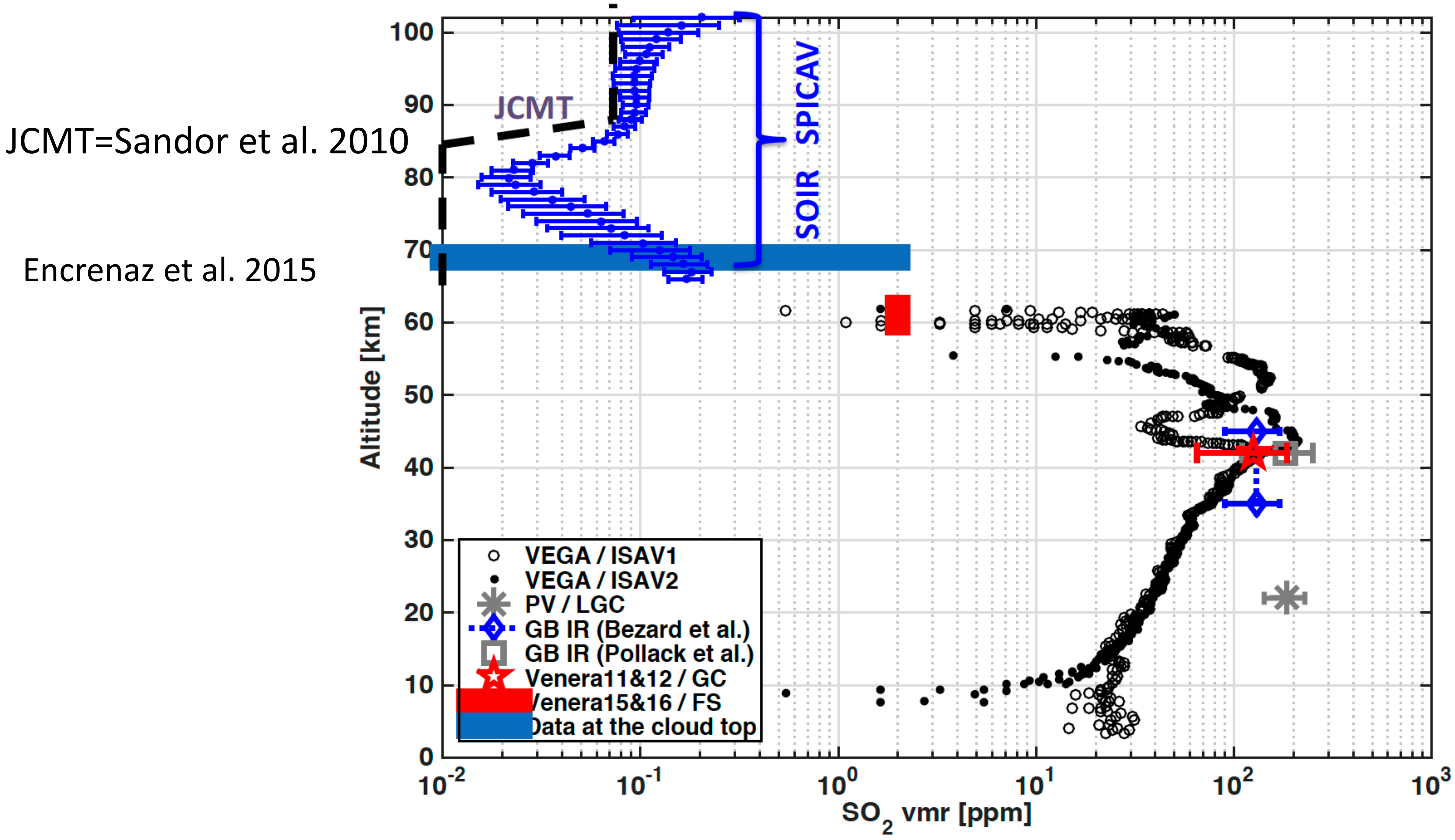

Figure credit: Belyaev D.A. (presented at 6MS3 symposium, IKI, Moscow 5–9 Oct. 2015).