

# Composition and Chemistry of the Neutral Atmosphere of Venus

E. Marcq (1), F. Mills (2), B. Sandor (3) and A.C. Vandaele (4)

(1) Univ. de Versailles Saint-Quentin/LATMOS, Guyancourt, France (emmanuel.marcq@latmos.ipsl.fr)

(2) Australian National Univ., Canberra, Australia; (3) Sp. Sci. Inst., Boulder, CO, USA; (4) Planetary Aeronomy, IASB-BIRA, Bruxelles, Belgium

## Introduction

With the pending ending of the ESA *Venus Express* mission after 8 years of scientific success, a new page in the *in situ* exploration of the inner solar system is on the verge of being turned. Considering how much our vision of Venus has been updated and refined thanks to it, the scientific community has decided to summarize our new picture of Venus in a dedicated book. This talk aims at presenting the structure and some contents of the *Composition and Chemistry of the Neutral Atmosphere* chapter.

## Emphasizing the variability

Prior to *Venus Express*-era, during the *Pioneer Venus* and *Venera* missions back in the 1980s, the focus of composition measurements in the Venusian atmosphere was on obtaining averaged mixing ratios of the bulk atmosphere and minor species. With the exception of SO<sub>2</sub> [4] and water, temporal and horizontal variabilities were not much investigated. Comparatively, vertical profiling was better studied and known, especially but not only thanks to the measurements of descent probes. The available computing power at that time also allowed little more than vertical 1D chemical modeling to support and interpret these observations.

This 30-year old “general picture” of Venusian atmospheric composition has not been overturned by *Venus Express*, but the amount of data gathered by its instruments, as well as the progress made by Earth-based telescopes and instruments have made increasingly difficult to reconcile individual observations of Venus with the aforementioned “average” knowledge of Venus. Evidence for variability in all four dimensions (temporal, vertical, latitudinal and longitudinal) has accumulated, so that we chose to base our reviews on these various types or variabilities, rather than e.g. on the compounds families or vertical structure as previously done [9, 3].

## Content Summary

### Vertical profiles

*Venus Express* has been the first space mission able to observe Venus in the night side infrared windows first discovered in 1984[1]. The VIRTIS (and to a lesser extent SPICAV) instrument suite was therefore designed to exploit these windows in order to derive mixing ratios of numerous minor constituents (HCl, HF, SO<sub>2</sub>) below the clouds, with some vertical profiling for CO and OCS in the lower atmosphere. Water vapor could even be profiled from the surface up to 30 km, and HDO/H<sub>2</sub>O mixing ratio could also be measured below the clouds.

Above the clouds, the occultation instruments SPICAV and SPICAV-SOIR on board *Venus Express* have greatly enhanced the vertical resolution and sensitivity of minor species profiling (albeit only on the night side with SPICAV or at dawn or dusk with SOIR), including some isotopes, notably HDO and H<sub>2</sub>O [5]. Sub-millimetric profiling from Earth-based observations enable profile retrievals of most of these species in the upper mesosphere using resolved line shapes. Chemistry, and especially photochemistry is also modeled with increasing detail, enabling quantitative interpretation of abundances and vertical profiles in terms of sinks and sources.

### Horizontal variability

Horizontal variability can be further distinguished along two axes: latitudinal and longitudinal – as far as the atmosphere is concerned, the longitudinal coordinate is often meaningfully replaced by the local solar time.

Latitudinal variability can be investigated with 2D – or even better 3D – chemical models[10]. It has also been measured both under the clouds for CO and OCS [8], and above the clouds for SO<sub>2</sub> and H<sub>2</sub>O. These variabilities are often symmetrical with respect to the

equator, leading to think that they result from the competition between chemical equilibrium and the general, meridional circulation.

Variability with respect to local solar time has been harder to evidence. None has been found below the clouds, in agreement with the fact that direct solar radiation is thought to play a negligible role below the clouds. Above the clouds, sub-millimeter observations of CO, SO<sub>2</sub> and SO have shown day side/night side asymmetry, consistently with their strong involvement with photochemical cycles.

## Temporal variability

The most striking temporal variability of atmospheric composition ever observed on Venus deals with sulfur compounds, namely SO and SO<sub>2</sub> above the clouds. All available observations (IR, sub-mm, UV) exhibit a strong temporal (and local) variability on various time scales, from a few hours up to several years. This variability is not yet fully understood, since the coupled dynamical/photochemical models do not succeed yet in simulating this variability – maybe future mesoscale models will be able to fill this gap.

Temporal variability of other minor species is not known with the same degree of certainty. Below the clouds, H<sub>2</sub>O and HDO may have varied [2, 6], but such an event has not been observed since then. Above the clouds, the same isotopes of water vapor, as well as carbon monoxide have been found to vary according to infrared and sub-millimeter observations [7].

## New detections and/or upper limits

Several minor constituents have also been discovered recently, e.g. ClO and H<sub>2</sub>SO<sub>4</sub> in the upper mesosphere, H<sub>2</sub>S in the lower atmosphere, NO in the cloud layer.

## Open Questions

We are still far from a full detailed understanding of the atmospheric chemistry of Venus. Here are some open questions that, according to us, may lead to significant changes in our knowledge of Venus once they are known in more detail: (1) Chemistry of the cloud region itself, where interactions between the particulate and gaseous phases add another complexity. It has also proven to be very hard to perform remote spectroscopic analysis therein. (2) Isotopic ratios, especially of noble gases and water vapor, contain the

key to the long-term history and evolution of the atmosphere. (3) Interactions with the surface and interior, especially regarding to yet unobserved volcanic outgassing. (4) Which laboratory studies are needed to better analyze existing and future observations of Venusian atmosphere?

## Acknowledgments

ACV acknowledges support from the Belgian Federal Science Policy Office and the European Space Agency (ESA - PRODEX program), from the “Interuniversity Attraction Poles” program financed by the Belgian government (Planet TOPERS), and from the FP7 EuroVenus project (G.A. 606798).

## References

- [1] Allen, D. A. and Crawford, J. W.: Nature, Vol. 307, pp. 222-224, 1984.
- [2] Bell, J. F. et al.: Spectroscopic observations of bright and dark emission features on the night side of Venus: Science, Vol. 252, pp. 1293-1296, 1993.
- [3] Esposito, L. W. et al.: Venus II – geology, geophysics, atmosphere and solar wind environment, University of Arizona Press, 1997.
- [4] Esposito, L. W. et al.: Sulfur dioxide at the Venus cloud tops, 1978-1986, Journ. of Geophys. Res., Vol. 93, pp. 5267-5276, 1988.
- [5] Fedorova, A. et al.: HDO and H<sub>2</sub>O vertical distributions and isotopic ratio in the Venus mesosphere by Solar Occultation at Infrared spectrometer on board Venus Express, Journ. of Geophys. Res. (Planets), Vol. 113, 2008.
- [6] Gurwell, M. A. et al.: SWAS observations of water vapor in the Venus mesosphere, Icarus, Vol. 188, pp. 288-304, 2007.
- [7] Krasnopolsky, V. A.: Chemical composition of Venus atmosphere and clouds: Some unsolved problems, Planet. and Sp. Sci., Vol.54, pp. 1352-1359, 2006.
- [8] Marcq, E. et al.: A latitudinal survey of CO, OCS, H<sub>2</sub>O and SO<sub>2</sub> in the lower atmosphere of Venus: Spectroscopic studies using VIRTIS-H, Journ. of Geophys. Res. (Planets), Vol. 113, 2008.
- [9] Von Zahn, U. et al.: Venus, University of Arizona Press, 1983.
- [10] Yung, Y. L. et al.: Evidence for carbonyl sulfide (OCS) conversion to CO in the lower atmosphere of Venus, Journ. of Geophys. Res. (Planets), Vol. 114, 2009.