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Vertical profiling of SO_2 and SO above Venus' clouds by SPICAV/SOIR solar occultations

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ABSTRACT

New measurements of sulfur dioxide (SO_2) and monoxide (SO) in the atmosphere of Venus by SPICAV/SOIR instrument onboard Venus Express orbiter provide ample statistics to study the behavior of these gases above Venus' clouds. The instrument (a set of three spectrometers) is capable to sound atmospheric structure above the clouds in several observation modes (nadir, solar and stellar occultations) either in the UV or in the near IR spectral ranges. We present the results from solar occultations in the absorption ranges of SO_2 (190–230 nm, and at 4 μm) and SO (190–230 nm). The dioxide was detected by the SOIR spectrometer at the altitudes of 65–80 km in the IR and by the SPICAV spectrometer at 85–105 km in the UV. The monoxide's absorption was measured only by SPICAV at 85–105 km. We analyzed 39 sessions of solar occultation, where boresights of both spectrometers are oriented identically, to provide complete vertical profiling of SO_2 of the Venus' mesosphere (65–105 km). Here we report the first firm detection and measurements of two SO_2 layers. In the lower layer SO_2 mixing ratio is within 0.02–0.5 ppmv. The upper layer, also conceivable from microwave measurements by Sandor et al. (Sandor, B.J., Todd Clancy, R., Moriarty-Schieven, G., Mills, F.P. [2010]. Icarus 208, 49–60) is characterized by SO_2 increasing with the altitude from 0.05 to 2 ppmv, and the $[SO_2]/[SO]$ ratio varying from 1 to 5. The presence of the high-altitude SO_x species could be explained by H_2SO_4 photodissociation under somewhat warmer temperature conditions in Venus mesosphere. At 90–100 km the content of the sulfur dioxide correlates with temperature increasing from 0.1 ppmv at 165–170 K to 0.5–1 ppmv at 190–192 K. It supports the hypothesis of SO_2 production by the evaporation of H_2SO_4 from droplets and its subsequent photolysis at around 100 km.

1. Introduction

Sulfur compounds are key components of Venus' atmosphere because the planet is totally covered by H_2SO_4 droplets clouds at altitudes 50–70 km. Any significant change in the SO_x oxides above and within the clouds affects the photochemistry in the mesosphere (Esposito et al., 1997). Moreover, it may be an indicator of geological activity on the planet: a single volcanic event could disturb the atmospheric circulation and increase the delivery of SO_x to the cloud top. Sulfur oxides actively participate in the photochemistry around Venus' clouds (Mills et al., 2007). SO_2 photodissociates under the effect of the solar radiation and, reversely, is formed by SO oxidation; further oxidation leads to SO_3 formation. Finally, in combination with H_2O it gives concentrated liquid sulfuric acid (~75% H_2SO_4).

The sulfur dioxide in the venusian atmosphere was first detected from Earth-based ultraviolet observations with a mixing ratio 0.02–0.5 ppm at the cloud top (Barker, 1979). Space-based identifications of SO_2 UV absorption followed soon from Pioneer Venus orbiter (PV) and International Ultraviolet Explorer (IUE). Continuous observations from the PV in 1978–1986 showed a steady decline of the cloud top SO_2 content from ~500 ppb down to 20–50 ppb about 2 years later (Esposito et al., 1988). The gas was detected in the 200–220 nm spectral range, where the absorption cross-sections of sulfur monoxide are even larger than those of the dioxide (Fig. 1). Later, on the basis of 1978–1988 IUE data Na et al. (1990) showed that SO_2 retrieval together with SO provided better fit than without SO. The SO mixing ratio was derived as 20 ± 10 ppb with $SO_2/SO \sim 10$ at the cloud top. In 1978–1991 UV rocket soundings gave average values of 80 ± 40 ppb for the

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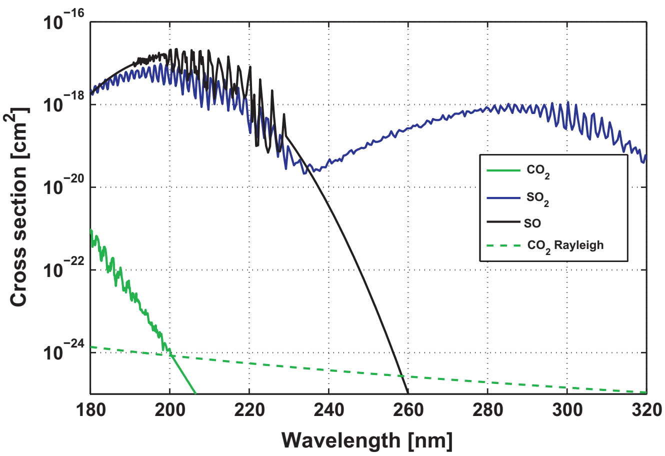

Fig. 1. Cross sections of molecular absorption and scattering (Rayleigh) that are taken into account in the UV range: CO_2 (solid green), SO_2 (solid blue), SO (solid black), Rayleigh scattering (dashed green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

dioxide and 12 ± 5 ppb for the monoxide, in good agreement with PV and IUE simultaneous observations (McClintock et al., 1994; Na et al., 1994). One more UV measurement was done in 1995 from the Hubble Space Telescope (HST) (Na and Esposito, 1995). They found the SO_2 abundance of 20 ± 10 ppb, which was lower than values obtained in 1978–1991 by a factor of 2–5, confirming again the decrease of SO_2.

The sulfur dioxide was also measured in the infrared spectral range by the Fourier Spectrometer onboard the Venera-15 orbiter. A strong dependence of the SO_2 content on latitude at the cloud top was reported: from 20 ppb in the equator to 0.5 ppm in the polar region (Zasova et al., 1993). These data were found consistent with PV and IUE results, taking into account different effective sounding altitudes.

Recently SO_x above Venus' clouds were measured in sub-mm range from JCMT telescope in 2004–2008 (Sandor et al., 2010). The profiles of measured lines are consistent with two layers of sulfur oxides in the Venus mesosphere: <10 ppb at 70–85 km; ~30 ppb of SO and ~70 ppb of SO_2 at 85–100 km. The first retrievals of SO_2 vertical profiles from the Venus Express (VEX) mission (Titov et al., 2006) were reported from solar occultations in the IR range (SOIR) (Belyaev et al., 2008). Mixing ratios around ~0.1 ppmv at high latitudes and ~1 ppmv at low latitudes were reported at 70 km with a fast decrease to an upper limit ~0.05 ppmv at 75–80 km. This latitudinal behavior is contradicts the Venera-15 results, but is confirmed by recent SPICAV-UV observations in nadir (Marcq et al., 2011a). On the average, the SO_2 content measured by SOIR at planetary terminator occurred to be higher than previous (1987–1995) results obtained mainly on the dayside in nadir viewing. SOIR's values are also confirmed by long-slit high-resolution spectrography CSHELL from the Earth, resulted in the mean SO_2 mixing ratio of 0.35 ± 0.05 ppm near 72 km (Krasnopolsky, 2010).

In the present work, we describe a new set of SO_2 and SO measurements by SPICAV and SOIR from the VEX orbiter with some update of the previous SOIR results and first SO_x observations by SPICAV in the UV range. SPICAV-UV is sensitive to sulfur oxides' absorption band at 190–230 nm and in solar occultation probes the altitudes 85–110 km. In the occultation mode the line-of-sights (LOS) of SPICAV and SOIR spectrometers are parallel allowing simultaneous measurements. Using these data we acquired vertical profiling of SO and SO_2 in Venus' mesosphere and compared it with recent observations and modeling.

2. Observations

The SPICAV instrument – Spectroscopy for Investigation of Characteristics of the Atmosphere of Venus (Bertaux et al., 2007a) – onboard Venus Express consists of three spectrometers: SPICAV UV and IR, and SOIR. For our study we use two of them: SPICAV-UV and SOIR. In the solar occultation mode they both operate simultaneously, sounding approximately the same target altitudes. At present, 39 sessions are available for SO_x analysis located mostly around the North Pole, and a few occultations in the equatorial region (Table 1). Solar eclipses from the VEX orbit occur at ~6:00 or 18:00 of the Venus local time (except very close to the North Pole) and we probe the twilight mesosphere. SO retrievals were performed from the SPICAV-UV observations together with SO_2 while SOIR is not able to detect the SO absorption. In the selected set of sessions the earliest one was on March 28, 2007 (orbit 341) and the latest one was on October 1, 2008 (orbit 894). It gave us the possibility to monitor the evolution of sulfur oxides' content during 1.5 years (2007–2008).

In the occultation mode the instrument registers the solar flux out of planetary atmosphere and later the flux, having passed through the different levels of the atmosphere. The ratio of the second flux to the first one determines the atmospheric transmission at fixed target altitude. This transmission (a relative quantity) is interpreted as due to the extinction from aerosols and gases, which can be identified by their spectral signature, and their quantity along the LOS determined. In this sense the occultation method

Table 1
List of joint SPICAV/SOIR occultations for SO_2 detection and associated parameters. The distance to the limb defines the vertical resolution.

Orbit #	Obs. #	Date	Latitude (°)	Loc. time (h)	Dist. to limb (km)
341	18	28/03/2007	82.3	17.3	3543
356	10	12/04/2007	84.1	07.4	3475
361	18	17/04/2007	79.1	06.8	3686
366	18	22/04/2007	71.5	06.5	4163
434	1	29/06/2007	29.2	18.0	5501
435	1	30/06/2007	72.3	18.1	2184
437	9	02/07/2007	74.9	18.2	2053
441	9	06/07/2007	78.5	18.3	1939
443	8	08/07/2007	79.9	18.4	1910
447	8	12/07/2007	82.2	18.7	1886
449	4	14/07/2007	83.3	18.9	1883
456	8	21/07/2007	86.5	20.3	1904
460	8	25/07/2007	87.7	22.6	1932
466	7	31/07/2007	86.6	03.1	1995
485	7	19/08/2007	68.9	05.5	2791
485	8	19/08/2007	11.2	06.0	7815
486	8	20/08/2007	17.9	05.9	7098
488	8	22/08/2007	34.5	05.9	5293
583	12	25/11/2007	84.1	07.5	2636
586	8	28/11/2007	82.0	07.1	2732
595	13	07/12/2007	16.3	06.0	8806
597	13	09/12/2007	34.7	06.1	4587
667	7	17/02/2008	78.3	18.3	2136
669	7	19/02/2008	79.8	18.4	2092
671	8	21/02/2008	81.2	18.6	2063
674	9	24/02/2008	83.0	18.8	2037
675	7	25/02/2008	83.6	18.9	2032
677	5	27/02/2008	84.6	19.2	2026
679	7	29/02/2008	85.6	19.6	2025
681	7	02/03/2008	86.5	20.0	2029
684	9	05/03/2008	87.6	22.0	2042
685	7	06/03/2008	87.8	22.8	2048
686	5	07/03/2008	87.8	23.8	2056
687	11	08/03/2008	87.7	00.8	2064
703	9	24/03/2008	77.5	05.2	2431
709	5	30/03/2008	68.0	05.5	3017
886	11	23/09/2008	76.0	18.2	1997
892	12	29/09/2008	81.0	18.5	1736
894	12	01/10/2008	82.2	18.6	1700