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S_3 and S_4 abundances and improved chemical kinetic model for Venus lower atmosphere

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Abstract

Mixing ratios of S_3 and S_4 are retrieved from the Venera 11 observations. The previous model for 0-47 km [4] is improved by (1) a test and inclusion of the S_4 cycle [9], (2) reduction of the H_2SO_4 and CO fluxes from the middle atmosphere by a factor of 4, (3) removal of sulfur flux from the middle atmosphere, (4) a closed boundary for OCS at the surface instead of a free parameter for the OCS density, and (5) some minor updates. The model results are briefly discussed.

1. Introduction

Chemistry in the lower atmosphere (0-47 km) is initiated by fluxes of photochemical products from the middle atmosphere, photolysis of S_3 and S_4, and thermochemistry in the lowest scale height. The greatest problem in the first kinetic model for the lower atmosphere [4] was a lack of rate coefficients for many reactions in the system that was partially compensated by some thermodynamic calculations and similarity considerations. Here we suggest some significant improvements to that model.

2. S_3 and S_4 abundances

Absorption spectra of S_3 and S_4 were obtained by [1, 3] and shown in Fig. 1. We scale the S_3 spectrum at 450-600 nm from [3] by a factor of 1.4 and use it and the S_4 spectrum from [1] for χ^2-fitting to true absorption spectra at 10-19 and 3-10 km on Venus extracted from the Venera 11 observations [6]. This fitting (Fig. 2) gives f_{S3} = 11 ± 3 ppt at 3-10 km and 18 ± 3 ppt at 10-19 km, f_{S4} = 4 ± 4 ppt at 3-10 km and 6 ± 2 ppt at 10-19 km, and a steep decrease in both S_3 and S_4 above 19 km.

We adopt variable yields of the S_3 and S_4 photolysis, which are assumed constant below the dissociation limits, and calculate the photolysis frequencies as functions of altitude using the observed Venera 11 spectra.

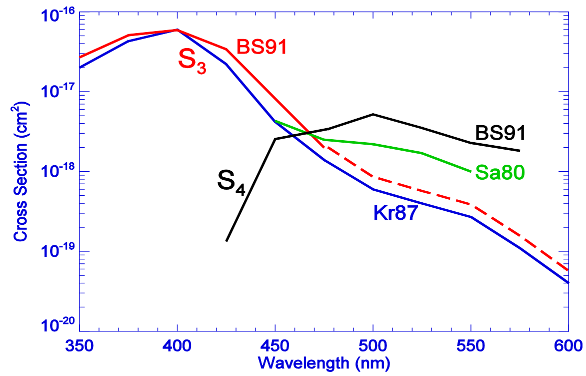

Fig. 1. S_3 and S_4 absorption cross sections from [1, 3]. The S_3 spectrum from [3] is scaled (dash line) for fitting the true absorption observed by Venera 11 [6].

3. Model

The observed abundances of SO_2, H_2O, HCl, and NO are used as the lower boundary conditions and cannot be checked by the model. The measured species that may be compared with the model results are CO, OCS, S_3, and S_4. The model includes 89 reactions of 28 species. Here we use the closed boundaries for CO and OCS at the surface instead of OCS as a free parameter at the surface in [4].

All photochemical models for the middle atmosphere [5, 7, 10] give rather similar productions of H_2SO_4, CO, and very low production of S_X. These products drive the chemistry in the lower atmosphere,

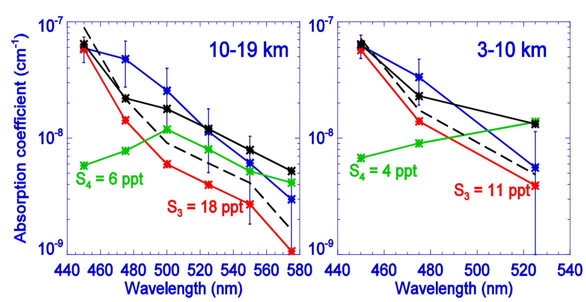

Fig. 2. χ^2-fits to the Venera 11 true absorption spectra [6] result in f_{S3}=18±3 ppt and f_{S4}=6±2 ppt at 10-19 km, f_{S3}=11±3 ppt and f_{S4}=4±4 ppt at 3-10 km.

and their significant reduction relative to [4] complicates the problem. Similar to [4], we adopt reactions

$SO_3 + OCS \rightarrow CO_2 + (SO)_2$ (1)

$(SO)_2 + OCS \rightarrow CO + SO_2 + S_2$ (2)

that deplete OCS and that have not been studied in the laboratory. An alternative S_4 cycle was suggested in [9] and remains untested:

$S_2 + S_2 + M \rightarrow S_4 + M$ (3)

$S_4 + h\nu \rightarrow S_3 + S$ (4)

$S_3 + h\nu \rightarrow S_2 + S$ (5)

$2(S + OCS \rightarrow CO + S_2)$ (6)

Net $2\ OCS \rightarrow 2\ CO + S_2$ (7)

We run our model with this cycle but without (1-2); the results disagree with the observations by orders of magnitude. However, inclusion of the S_4 cycle into our model improves its agreement with the measurements (Fig. 3).

Calculated profiles of abundant species in the model are shown in Fig. 4. Chemistry of the lower atmosphere is driven by sulfur, the OC=S bond is comparable with those in S_X, and the calculated sum OCS + S_X is constant at 20 ppm up to 47 km. (Here $S_X = \Sigma n S_n$.) The reduced sulfur OCS+S_X is formed by

$SO + SO \rightarrow SO_2 + S$ (8),

and exchange of S between OCS and S_X exceed the rate of (8) by two orders of magnitude. S_8 dominates near 47 km with a mixing ratio of 20/8=2.5 ppm. It is generally believed that sulfur aerosol is formed photochemically near the cloud tops [8]. However, the models do not support this hypothesis, and free sulfur is formed in the lower atmosphere, moves up by eddy diffusion and condenses near 50 km. It cannot be the NUV absorber that steeply decreases from 60 to 57 km according to the Venera 14 observations [2]; the sulfur behavior is opposite.

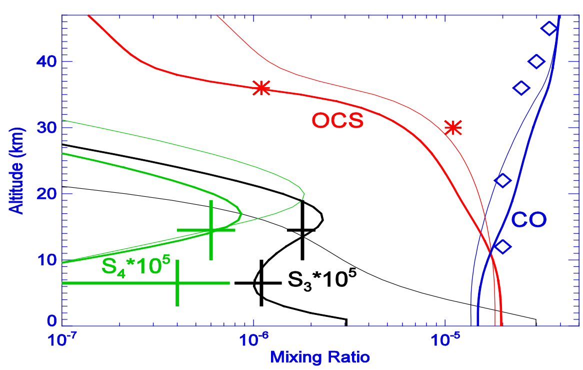

Fig. 3. Calculated profiles of CO, OCS, S_3, and S_4 in the basic model (solid lines) and that without the S_4 cycle are compared with observations.

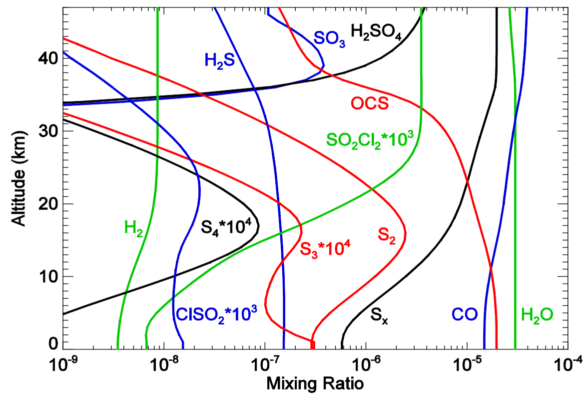

Fig. 4. Calculated chemical composition of Venus' atmosphere below the clouds. Mixing ratios of SO_2 (130 ppm), HCl (0.5 ppm), and NO (5.5 ppb) are constant and not shown. $S_x = \sum nS_n$ for n = 1 to 8.

OCS+CO is also constant in the lower atmosphere with a mixing ratio of 35 ppm. The calculated profiles for both species are in good agreement with the observations (Fig. 3). Gaseous H_2SO_4 peaks at 3.8 ppm near 47 km with a layer halfwidth of 6 km, in accord with the observations. The calculated H_2S varies from 150 ppb near the surface to 32 ppb at 47 km and does not support some controversial detections. H_2 increases from 3.5 ppb to 8 ppb at 47 km (Fig. 4).

The atmospheric sulfur cycles (see [4]) have been properly revised to account for the recent observations and models.

Acknowledgement

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