Disulfur dioxide and its NUV absorption in the photochemical model of Venus atmosphere

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Abstract

The Venus photochemical model (Krasnopolsky 2012) is updated by the data on S$_2$O$_2$ formation and photolysis (Frandsen et al. 2016) and improved densities of H$_2$O, OCS, and H$_2$ at 47 km (Krasnopolsky 2013). The basic model and four versions with small deviations in eddy diffusion and SO$_2$ at 47 km are presented and agree with the observed variations of CO, H$_2$O, SO$_2$, SO, and OCS. Three methods are used to evaluate S$_2$O$_2$ abundance sufficient for the NUV absorption, and the required S$_2$O$_2$ exceeds the model prediction by a factor of 200. The SO profile by Na et al. (1994) with 12 ppb at 64-95 km significantly exceeds the model below 74 km. If SO $\approx$ 12 ppb at 64 km, then S$_2$O$_2$ contributes to but does not completely explain the NUV absorption.

1. Introduction

Frandsen et al. (2016) proved that S$_2$O$_2$ is formed by SO + SO + M as cis- and trans-OSSO isomers that dissociate to SO and calculated their absorption spectra. Using the SO abundances of 12 ppb at 64-95 km observed by Na et al. (1994), they calculated abundances of OSSO that appear sufficient to explain the NUV absorption of Venus at 320-500 nm. We will implement the findings by Frandsen et al. (2016) into our photochemical model (Krasnopolsky 2012, Paper I), update the model using the chemical kinetic model (Krasnopolsky 2013), and test the hypothesis of OSSO as the NUV absorber.

2. Updated photochemical model

It was assumed in Paper I that S$_2$O$_2$ is formed as the lowest energy isomer S=S=O$_2$ that dissociates to S + SO$_2$. The formation of OSSO and its dissociation to SO + SO significantly affect the sulfur chemistry in the model that also adopts the OSSO formation and dissociation reaction rates from Frandsen et al. (2016). The model is updated using mixing ratios of H$_2$O = 26 ppm, OCS =140 ppb, and H$_2$ = 8.5 ppb at 47 km from the chemical kinetic model (Krasnopolsky 2013) as the lower boundary conditions. Similar to Paper I, a basic model and four versions with minor variations of eddy diffusion and SO$_2$ at the lower boundary were calculated (Table). Here eddy diffusion is 7300 cm$^2$ s$^{-1}$ below $h_e$, increasing to 10$^7$ cm$^2$ s$^{-1}$ at 100 km above $h_e$.

Table. Some data from five versions of the model

<table>
<thead>
<tr>
<th>$h_e$ km</th>
<th>SO$_2$ ppm</th>
<th>H$_2$O ppm</th>
<th>SO$_2$ ppb</th>
<th>SO ppb</th>
<th>S$_2$O$_2$+hv km$^{-2}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>9.7</td>
<td>3.11</td>
<td>128</td>
<td>10.1</td>
<td>3.91+13</td>
</tr>
<tr>
<td>57</td>
<td>9.7</td>
<td>4.38</td>
<td>577</td>
<td>43.4</td>
<td>5.39+13</td>
</tr>
<tr>
<td>65</td>
<td>9.7</td>
<td>2.90</td>
<td>57</td>
<td>2.44</td>
<td>5.99+13</td>
</tr>
<tr>
<td>60</td>
<td>8.7</td>
<td>5.36</td>
<td>70</td>
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<td>2.77+13</td>
</tr>
<tr>
<td>60</td>
<td>10.7</td>
<td>1.48</td>
<td>342</td>
<td>25</td>
<td>5.46+13</td>
</tr>
</tbody>
</table>

Fig. 1. Basic sulfur species: model results (solid, short and long dashes for $h_e$ = 60, 57, and 65 km, respectively) and observations. S$_a$ refers to total number of sulfur atoms in the aerosol. Observations of SO by Na et al. (1994) and Jessup et al. (2015) are (6) and (7).
of ≈30 and do not require volcanism. Variations of H2O in the model and observations are compared in Fig. 2. Again, there is a good agreement between the model and observations.

Fig. 2. Vertical profiles of H2O for SO2 = 8.7, 9.7, and 10.7 ppm at 47 km (red, blue, and green lines) are compared with the observations.

3. NUV absorption by OSSO

The calculated column photolysis rate of OSSO is 3.9×10^13 cm^{-2} s^{-1} and peaks at 68 km in a layer of 4 km thick. The NUV absorption at 320-500 nm (Fig. 3) removes 1.9×10^{16} cm^{-2} s^{-1} solar photons and exceeds the OSSO photolysis in the model by a factor of 500. The calculated OSSO column is 2.13×10^{14} cm^{-2} with the cis-to-trans isomer ratio of 0.82/0.18.

Fig. 3. Observed spectrum of Venus (blue, Barker et al. 1975) is compared with OSSO absorption in a thin layer (red) and for uniformly mixed absorber (green) with the isomer proportion 0.82/0.18 and 0.7/0.3 (solid and dashed curves, respectively). The OSSO abundances in the models are chosen to fit the observation at 350 nm.

The observed spectral reflectivity of Venus is compared with that of OSSO in Fig. 3. The red curve is for a thin absorbing layer above the clouds with OSSO = 2.8×10^{16} cm^{-2} exceeding the model value by a factor of 130. The green curve is for OSSO = 4×10^{16} cm^{-2} uniformly mixed in the upper cloud layer. (The cis-to-trans ratio is 0.7/0.3 in production and 0.82/0.18 in abundances because of the weaker photolysis of cis-OSSO.) This abundance exceeds the model value by a factor of 190. Frandsen et al. (2016) calculated the OSSO densities using SO = 12 ppb at 64-95 km observed by Na et al. (1994). This SO exceeds the recent observations by Jessup et al. (2015, 6.5, 2, and 1 ppb at 74-81 km, Fig. 1) and the model values below 74 km. Even SO from Na et al. (1994) results in an absorption that is weaker than that observed by a factor of 3. The spectral fit by OSSO to the observed NUV absorption is not perfect as well. Even if SO from Na et al. (1994) is valid below 74 km, then OSSO contributes to but does not completely explain the NUV absorption.

Na and Esposito (1997) proposed S2O as the NUV absorber. They calculated [S2O] ≈ 5×10^9 cm^{-3} at 64 km, close to that at 47-60 km in our model. However, absorption spectra of gaseous S2O are lacking. Strong arguments in favour of FeCl3 diluted to ≈1% in the droplets of sulphuric acid in the upper cloud layer may be found in Krasnopolsky (2017). This species explains the NUV absorption, though contribution of other candidates is not ruled out.

Acknowledgement

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References