THE O₂ DAYGLOW OBSERVATIONS WITH THE SPICAM IR EXPERIMENT ON MARS-EXPRESS.

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Introduction:
Ozone is one of the most chemically reactive species of the Martian atmosphere. Study of temporal and space ozone variability along with water vapor variability is necessary to improve photochemical models which have to explain the CO₂ atmosphere stability phenomenon. The point is that solar UV radiation dissociates CO₂ into CO and O, but their recombination is a very slow process in comparison with O recombination into O₂. So, O₂ and CO concentrations are expected to be higher than those that were measured. A stably high CO₂ concentration maintenance is associated with a chemistry involving “odd hydrogen” species (H, OH, HO₂…), as OH can easily react with CO₂ thus forming CO₂ [1]. These “odd hydrogen” species, with the exception of H₂O₂, had not been directly observed yet. As is known, O₃ can be destroyed by odd hydrogen thereby it can be a sensitive tracer to HOx species.

Observations:
The SPICAM IR spectrometer onboard Mars express mission, launched in 2003, is capable to measure ozone concentration in the Martian atmosphere using observations of O₂ molecule emission at 1.27 μm [2].

It covers the spectral range of 1-1.7 μm with spectral resolution of 0.5-1.2nm. The field of view of the spectrometer in the nadir-limb mode is 1° that corresponds to 15-100 km for limb observations depending on the distance to limb and ~5 km near the pericenter in nadir.

In this work we present results of limb and nadir observations of the O₂ emission and vertical retrieval of ozone profile based on SPICAM IR data. In the limb observation mode spacecraft scans a disc of the planet, its orientation remaining in an inertial attitude. From January 2004 to April 2010 there were made about 600 limb observations in IR range, but only 105 of them were analyzed, as most part of observations were made as a full spectrum with a low sampling. In case of nadir all dataset from 2004 to 2010 has been analyzed.

O₃ photolysis:
Ozone can photodissociate in the following reactions:

\[ \text{O}_3 + \text{hv} \rightarrow \text{O}_2(\Delta\text{g}) + \text{O}_2(\text{a}_\text{g}) \] (1)

\[ \text{O}_3 + \text{hv} \rightarrow \text{O}(\text{P}) + \text{O}_2(\text{X}\Sigma_g) \] (2).

The effectiveness of the first reaction is equal to 90%. Photodissociation rate coefficient depends on the solar flux value, solar zenith angle, temperature [3]. For the radiative lifetime we have used the value \( \tau = 4566 \text{s} \) [4].

Excited O₂ molecule can be deactivated through emission:

\[ \text{O}_2(\text{a}_\text{g}) \rightarrow \text{O}_2(\text{X}\Sigma_g) + \text{hv} \] (3)
or collision:

\[ \text{O}_2(\text{a}_\text{g}) + \text{CO}_2 \rightarrow \text{O}_2(\text{X}\Sigma_g) + \text{CO}_2. \] (4)

Emission (3) occurs at the wavelength 1.27μm and 1.58μm, though the second is 45 weaker while being measured in the laboratory.

For the rate constant of deactivation through collision with CO₂ we have used a value \( k = 10^{-19}\text{cm}^3\text{molecules}^{-1}\text{s}^{-1} \) [5].

The O₂ intensity in MR can be expressed as:

\[ 4\pi f(MR) = 10^{-18} \int_0^\infty \frac{[O_3]dz}{1 + k[\text{CO}_2]}, \] (5)

Vertical distribution of the O₂ emission and O₃

The retrieval of the O₂ on limb based on an algorithm presented in [6] but with some key modifications. To receive the intensity of the O₂ emission in the 1.27μm band we should take into account some spectral features in this range such as solar Fraunhofer line at 1262, 1268 and 1268nm, CO₂ ice absorption at 1262-1269nm.

Ozone profile can be retrieved from O₂ emission slant profile (Eq. 5) using Abel inversion scheme. To decrease an amplification of the noise of obtained profiles we have used a Tikhonov regularization algorithm (for more details see [7]).

Some examples of retrieved O₃ profiles are shown on the Figure 1 and 2.

Seasonal distribution of the O₂ emission:
We present also the results of O₂ emission observations by SPICAM IR [6] for 3.5 Martian years (Fig.3) from January 2004 (MY26) to November 2010 (MY30). The year-to-year variations of the O₂ dayglow could relate to the local time variations during the observations as well as true seasonal variations of ozone.

As it was mentioned above (Eq. 5), the O₂ emission can be expressed through O₃ concentration, O₂ radiative lifetime and rate constant k of deactivation through collision with CO₂. The latter is known with great uncertainty. To constrain this constant we have made a theoretical O₂ emission map for the same latitudes, longitudes,
local times and solar longitudes based on LMD GCM model (version 4.3) as at those SPICAM observations were made [3,8]. A detailed comparison of these two maps can give us a restriction on the value of the rate constant of deactivation ($k \approx 0.5 \times 10^{-20} \text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$).

Figure 1. Comparison of observed (solid line) and modeled (dashed line) ozone vertical profiles for perihelion period (a,b), for high northern latitudes during vernal equinox (c,d), for high southern latitudes during winter solstice (e,f).

Figure 2. Comparison of observed (solid line) and modeled (dashed line) ozone vertical profiles for high northern latitudes in summer (a,b), for mid northern latitudes in spring (c,d), for high northern latitudes in spring (e,f).

References:
Figure 3. Seasonal distribution of the O$_2$ emission observed by SPICAM from $L_s$ 330° MY26 (January 2004) to $L_s$ 120° MY30 (November 2010).