Simplified Relations for the Martian Nighttime Hydroxyl Layer Suitable for Interpretation of Observations

Dmitry Shaposhnikov[1], Mykhaylo Grygalashvyly[2], Alexander S. Medvedev[2], Gerd Reinhold Sonnemann[2], and Paul Hartogh[2]

Introduction

Observations of excited hydroxyl (OH*) emissions are broadly used for inferring information about atmospheric dynamics and composition. It plays an important role in the photochemical balance and is affected by transport and mixing processes. We present several analytical approximations for characterizing the hydroxyl layer in the Martian atmosphere. They include OH* number density at the maximum and the height of the peak, along with the relations for assessing different impacts on the OH* layer at nighttime conditions. These characteristics are determined by the ambient temperature, atomic oxygen concentration and their vertical gradients. The derived relations can be used for analysis of airglow measurements and interpretation of its variations.

Analytical Approaches

Assuming the photochemical equilibrium for excited hydroxyl in the vicinity of OH^* layer (~40-60 km) at nighttime conditions (García-Muñoz et al., 2005) and omitting the reaction hydroperoxy radicals (HO_2) with atomic oxygen as negligible for population of vibrationally excited hydroxyl (Xu et al., 2012; García-Muñoz et al., 2005) we start from almost full equation for vibrationally exited hydroxyl:

$$[OH_v] \approx \frac{\left(\begin{array}{c} f_v r_1 [H][O_3] + \sum_{v'=v+1}^{9} A_{v'v}[OH_{v'}][CO_2] + \\ \sum_{v'=v+1}^{9} G_{v'v}[OH_{v'}][N_2] + \sum_{v'=v+1}^{9} B_{v'v}[OH_{v'}][O_2] \\ + \sum_{v'=v+1}^{9} D_{v'v}[OH_{v'}][O] + \sum_{v'=v+1}^{9} E_{v'v}[OH_{v'}] \end{array} \right)}{\left(\begin{array}{c} \sum_{v''=0}^{v-1} A_{vv''}[CO_2] + \sum_{v''=0}^{v-1} G_{vv''}[N_2] + \\ \sum_{v''=0}^{v-1} B_{vv''}[O_2] + \sum_{v''=0}^{v-1} D_{vv''}[O] + \sum_{v''=0}^{v-1} E_{vv''} + \\ + r_4(v)[O] \end{array} \right)}, (1)$$

where v is vibrational number (here and after $v < v'$; $v'' < v$); f_v is the nascent distributions, r – reaction rates, A, B, G, and D are the quenching coefficients for CO_2, O_2, N_2, and O, respectively. All used reactions and processes are collected in Table 1. The square brackets, here and after, denote number density of given chemical constituents.

Writing the numeric value of the reaction rate explicitly and reorganizing (1), we obtain

$$[OH_v] \approx \varepsilon \gamma_v [O] T^{-2.4} M, (2)$$

where $\varepsilon = 6.1 \cdot 10^{-24} \cdot 298^{2.4} \beta$ and $\gamma_v = \frac{f_v + \sum_{v'=v+1}^{v'=9} \gamma_{v'} C_{v'v}}{\sum_{v''=0}^{v''=v-1} C_{vv''}}$, $\left(f_{9<v<5} = 0, v < v', v'' < v\right)$, M is air density.

The theoretical solutions derived above assume for quenching and spontaneous emission processes multi-quantum relaxation, at which transitions occurs from all vibrational levels above to all lower one. To date, not all multi-quantum quenching coefficients for CO_2 and N_2 are known. Currently known just so-called collisional cascade quenching rates, when for all vibrational levels assumed transition to one level below.

The input profiles, were taken from the MCD, which is based on simulations with the Laboratoire de Météorologie Dynamique General Circulation Model (LMD-GCM) (Forget et al., 1999). The MCD contains distributions of minor gases in the Martian atmosphere, including O_3 (Lefèvre et al., 2004; 2008), that is directly involved in OH^* production, H_2O (Navarro et al., 2014), which is the principal source of odd-hydrogens, and variations of other long-lived species (CO_2, N_2) involved in quenching processes (Forget et al., 1998, 2008).

Tables and Figures

	Reactions	Coefficients
1	$H + O_3 \xrightarrow{f_v r_1} OH_{v=5,\dots,9} + O_2$	$r_1 = 1.4 \cdot 10^{-10} exp\left(\frac{-470}{T}\right)$ $f_{v=9,\dots,5} = 0.47, 0.34, 0.15, 0.03, 0.01$
2	$O + O_2 + CO_2 \rightarrow O_3 + CO_2$	$r_2 = 6.1 \cdot 10^{-34} (298/T)^{2.4}$
3	$O + O_3 \rightarrow 2O_2$	$r_3 = 8 \cdot 10^{-12} exp\left(\frac{-2060}{T}\right)$
4	$O + OH_{v=1,..,9} \rightarrow O_2 + H$	$r_4(v = 9, \dots, 1) = (5.42, 4.8, 4.42, 4, 3.77, 4.43, 3.74, 3, 3.15) \cdot 10^{-11}$
5	$OH_v + CO_2, O_2, N_2, O \rightarrow OH_{v'<v} + CO_2$	$A_{vv'}, B_{vv'}, G_{vv'}, D_{vv'}$ See text
6	$OH_v \rightarrow OH_{v'<v} + hv$	$E_{vv'}$

Table 1. List and nomenclature of reaction rates, quenching coefficients, spontaneous emission coefficients (references: [1,2,3]Burkholder et al. (2020), [1,5]Adler-Golden (1997), [4,5]Caridade et al. (2013), [5]Makhlouf et al. (1995), [5]Krasnopolsky (2013), [6]Xu et al. (2012)).

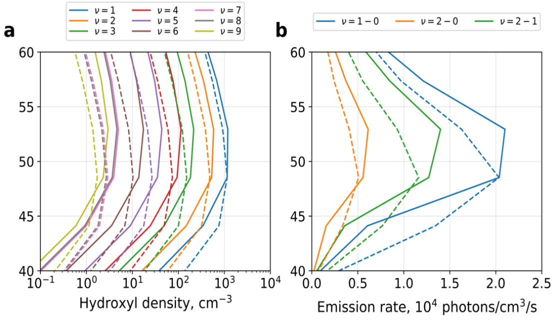

Figure 1. Nighttime averaged zonal mean, averaged over 70°N – 90°N, and L_s 265°-320° (in order to obtain colocation with Clancy et al. (2013) observations): (a) $OH_{v=1,\dots,9}$, calculated by Eq. (1) (solid lines) and calculated by Eq. (2) (dashed lines), (b) volume emission calculated by Eq. (1) and (2) (solid and dashed lines, respectively) for vibrational transitions 1-0 (blue), 2-1 (green), and 2-0 (red).

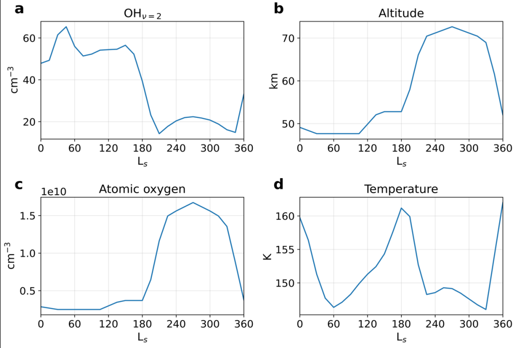

Figure 2. Nighttime mean one month sliding averaged values at peak of the $OH_{v=2}$ layer calculated by Eq. (1) at middle (40°N) latitudes: a) $[OH_{v=2}]$, b) height of peak, c) [O], and d) temperature.

Summary and Conclusions

The simplified relations for OH* in Martian atmosphere at nighttime conditions for height of OH* peak and concentration at peak were derived with assumptions that:

1) quenching by carbon dioxide, molecular oxygen, and molecular nitrogen dominate over quenching by atomic oxygen and spontaneous emission;
2) ozone is in photochemical equilibrium in the vicinity of OH* layer.

At this approximation, nighttime [OH*] at peak is proportional to the atomic oxygen concentration and negative power of temperature. The [OH*] in the vicinity OH* layer is directly proportional to the pressure (i.e., inversely to the layer altitude). Hence OH* emission, which comes almost from vicinity of peak, anticorrelates with the height of the OH* layer. OH* layer on Mars may reveal annual and semi-annual cycles, as the result of annual (semi-annual) cycles of temperature, air number density, [O], and their superpositions. The expressions for assessment of relative variation of OH* due to variations of temperature, [O], and concentration of air were obtained. All of these expressions can be useful for analysis and interpretation of hydroxyl emission observations.

[1] Moscow Institute of Physics and Technology, Moscow, Russia
[2] Max Planck Institute for Solar System Research, Göttingen, Germany

shaposhnikov@phystech.edu
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mars.mipt.ru

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