

SIMULATIONS OF THE O₂ IR ATMOSPHERIC EMISSIONS IN THE MARTIAN ATMOSPHERE.

M.-È. Gagné, *Department of Physics, University of Toronto, Toronto, Canada, (megagne@atmosph.physics.utoronto.ca)*,
K. Strong, *Department of Physics, University of Toronto, Toronto, Canada, (strong@atmosph.physics.utoronto.ca)*,
S. M. L. Melo, *Department of Space Science, Canadian Space Agency, Saint-Hubert, Quebec, Canada (stella.melo@asc-csa.space.gc.ca)*.

Introduction

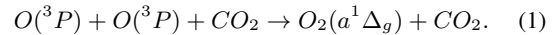
The (0-0) transition of the Infrared Atmospheric band system ($a^1\Delta_g - X^3\Sigma_g^-$) of O₂ at 1.27 μm was first detected in the Mars dayglow by Noxon et al. [1976]. The typical intensity of this band is about 1-30 MR [Slanger et al., 2008]. Since 2003, the SPectroscopy for the Investigation of the Atmosphere of Mars (SPICAM) experiment on board Mars Express provides systematic measurements of the emission such that a global and temporal distribution of the emission has been produced [Fedorova et al., 2006a]. Recently, the Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité (OMEGA) instrument, also on Mars Express, observed for the first time the O₂ IR emission at nighttime [Gondet et al., 2010]. The feature was also measured by the Mars Climate Sounder (MCS) on the Mars Reconnaissance Orbiter (MRO) around the same period [McCleese and Kass, 2010].

On Venus, which has a similar atmospheric composition to the Mars atmosphere at the airglow altitude, i.e. around 95 km on Venus as compared to 65 km for Mars, the nightglow emissions from the O₂ 1.27- μm band have been observed for over 30 years [Connes et al., 1979]. The measurements show that the day and night airglow from the O₂($a^1\Delta_g$) state are of comparable intensities: the nightglow emissions can reach intensities of ~ 5 MR [Ohtsuki et al., 2005], while the dayglow average intensity is on the order of 1-2 MR [Slanger et al., 2008].

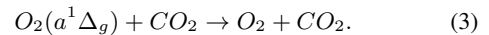
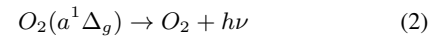
One major difficulty in properly reproducing the observed global distribution and intensity range of the O₂ IR airglow in an atmosphere dominated by CO₂ is the lack of knowledge on the photochemical parameters associated with the emission, mostly regarding the quenching of the excited state by CO₂. In this paper, we use kinetic parameters reported in the literature to estimate the intensity of the O₂($a^1\Delta_g, 0 - X^3\Sigma_g^-, 0$) band emissions at night and daytime in the Martian atmosphere and to evaluate the sensitivity of the emission features to these parameters. The simulations shown here use profiles of atomic oxygen and CO₂ density, and temperature generated by the Laboratoire de Météorologie Dynamique Mars Global Circulation Model (LMD-MGCM) at midnight (for nighttime) and noon (for daytime), and for different seasons [??].

O₂ photochemistry

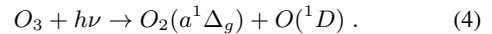
At night, the O₂($a^1\Delta_g$) state is produced through the three-body recombination of oxygen atoms:



The excited state can then either emit a photon by radiative decay, reaction (2), or be quenched by collision with another molecule, most probably CO₂, resulting in the loss of the excited state, reaction (3):



The daytime production of the excited state, O₂($a^1\Delta_g$), is mainly determined by photodissociation of ozone:



The contribution to the O₂($a^1\Delta_g$) formation from the recombination of oxygen atoms, reaction (1), is less important during daytime, i.e. it accounts for 10% or less, but it is the major production mechanism at night.

Simulations

In our simulations, we use a value of $1.2 \times 10^{-32} \times (300/T)^2 \text{ cm}^6 \text{ s}^{-1}$ for the rate coefficient of the three-body recombination reaction (1) [Krasnopolsky, 1995]. The lifetime used in our model for O₂($a^1\Delta_g$) is 4,470 s [Lafferty et al., 1998]. The production yield (α) of the excited state and its removal rate by CO₂ (k_{CO_2}) are not well-determined; hence our simulations will use different values taken from the literature to investigate which sets of parameters best reproduce the observations. Also, we chose the photolysis rate for O₃ of $3 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$ with a yield of 0.92 for the ($a^1\Delta_g$) state of O₂ [Krasnopolsky, 2006].

Figure 1 show the latitudinal variations of dayglow intensity at different seasons, displayed as a function of aerocentric longitude L_S , for three simulated cases. In brief, case 1 corresponds to the parameters used by Krasnopolsky [2009] in a photochemical model to reproduce the O₂ 1.27- μm emission in the Mars atmosphere from Earth-based observations ($\alpha = 0.67$, $k_{CO_2} = 5 \times 10^{-21} \text{ cm}^3 \text{ s}^{-1}$). The yield and quenching rate of Krasnopolsky [2010] derived from Venus

observations from the Earth are used in case 2 ($\alpha = 0.7$, $k_{CO_2} = 10^{-20} \text{ cm}^3 \text{ s}^{-1}$). Case 3 uses the best-fit parameters to the observations from the Visible and Infrared Thermal Imaging Spectrometer (VIRTIS) instrument on Venus Express as described in García Muñoz et al. [2009] ($\alpha = 0.5$, $k_{CO_2} = 2 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$). The trends for the three cases are similar: the intensity is relatively low and constant in a 80° band centered over the Equator. Then, the intensities increase towards the poles, except at the beginning of the summer season in each hemisphere $-L_S = 90\text{-}120^\circ$ for the North polar region, i.e. above 50° N , and $L_S = 270\text{-}300^\circ$ for the South polar region, i.e. above 50° S — where the intensities decrease slightly. However, the intensity maxima from case 1 to case 3 diminish, a consequence of stronger quenching by CO₂ in case 3 than in case 2, and than in case 1. The effect of quenching by CO₂ on the excited state is to reduce the emission rate from the excited state, as expected, and the effect is clearly seen in these simulations. Since the production of O₂(a¹Δ_g) during daytime is mainly through photodissociation of ozone, reaction (4), the effect of the production yield from reaction 1 on the emission intensity is negligible. This fact has been tested in other calculations (not shown here) and strongly suggests that the dominant kinetic parameter for daytime O₂(a¹Δ_g) emission intensity is the quenching rate by CO₂ of the excited state.

If we compare the results from these simulations with the observations made by SPICAM [Fedorova et al., 2006a,b], the intensity range from case 1 reproduces the measurements with better agreement than the two other cases. Case 3 does not produce intensities in the 30-MR range, which are the high-end values of the intensity range observed. As for case 2, the intensity values are slightly lower than the SPICAM results. In general, the trends and values of the intensity from the O₂ 1.27-μm emission from case 1 matches well the observations, although even for this case, the intensities from our model simulations are typically lower by a few megaRayleigh as compared to the observations. Moreover, some discrepancies occur for $L_S = 0\text{-}30^\circ$ where the observations show an increase of intensity from 30° to 55° S and then a decrease towards the pole, while our results yield a steep increase towards the pole above 40° S . This situation is repeated for $L_S = 180\text{-}210^\circ$ where the intensity peaks at 70° N in the SPICAM measurements as opposed to a steady increase northward of 40° N in our model.

We note that the coverage of the SPICAM observations in the published results does not extend beyond latitudes above 60° during the fall and winter seasons in each hemisphere, and this is where and when we would expect the strongest O₂ IR emissions. It is also important to point out that our simulations are performed with averages over 30° of L_S , in contrast to the singularity in time of the SPICAM measurements. Our model results then represent average conditions over a specific year, Martian year 24 for instance, which were considered to

exhibit average dust conditions. Therefore, since we are not using in our model the specific atmospheric conditions observed during the SPICAM observations, it is outside our capability to decide whether case 1 or case 2 is the best case scenario. Nevertheless, the fact that our simulations from the case 1 scenario reproduce the SPICAM observations closely gives us confidence in our O₂ photochemistry model.

We now present our predictions for the nighttime O₂ 1.27-μm emission following the parameters used previously for the dayglow simulations. The latitudinal trends of the intensity at the onset of each season are shown in Figure 2. Throughout the year, for all simulated cases, the intensity between 50° N and 50° S is on the order of 10^{-2} MR, which is relatively low compared to the maxima over the poles. The O₂ emission is stronger over the North polar cap in wintertime with intensities reaching above 1 MR. A maximum is also reached during the Southern hemisphere winter with values approaching 1 MR.

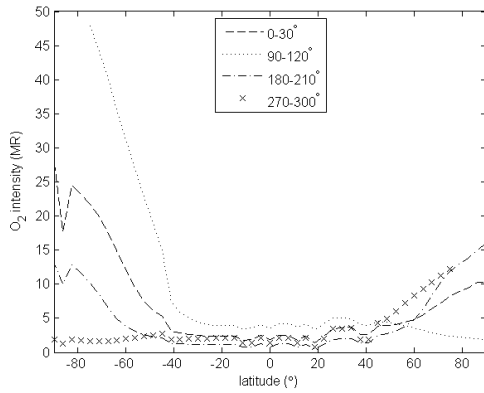
For nighttime conditions, the determining factor seems to be the production yield from the recombination of oxygen atoms. On simulations where we use a constant yield, say $\alpha = 0.7$, increasing the quenching rate from $k_{CO_2} = 5 \times 10^{-21} \text{ cm}^3 \text{ s}^{-1}$ (case 1) to $k_{CO_2} = 2 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$ (case 3) results in minimal variations of the emission intensity (simulations not shown here). This is due to the fact that, at night, reaction (1) is the major production mechanism for the O₂(a¹Δ_g) state and that determines the quantity of this excited state present in the atmosphere that can undergo radiative relaxation. Small variations in the quenching rate are then negligible while changing the production yield, even by a few percent, changes the emission intensity by as much as a few 10^{-1} MR.

The latitudinal trend for each season is similar for daytime and nighttime conditions. However, at nighttime the intensity maxima are reached over the North Pole, while during the day the highest values are found over the South Pole.

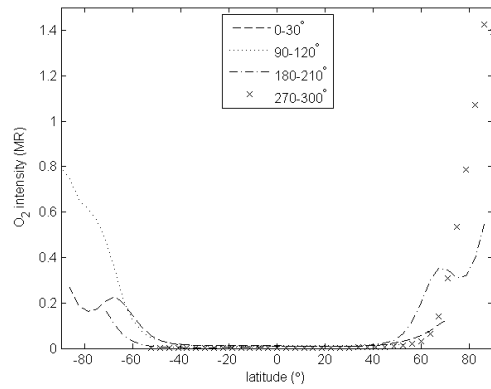
Summary

We have investigated the expected latitudinal distribution of the 1.27-μm emission of O₂ at four different seasons in the Mars atmosphere using different production yields and quenching rates of the O₂(a¹Δ_g) state. From the simulations of the emission for Mars atmospheric conditions and comparisons with SPICAM observations, we conclude that a smaller quenching rate coefficient by CO₂ of the order of $5 \times 10^{-21} \text{ cm}^3 \text{ s}^{-1}$ is more favourable for reproducing the highest intensities observed in the polar regions during the day. We also share the opinion of the cited authors [Krasnopolsky, 2009, 2010], in using a high production yield of about 0.7, for the production of the excited state follow-

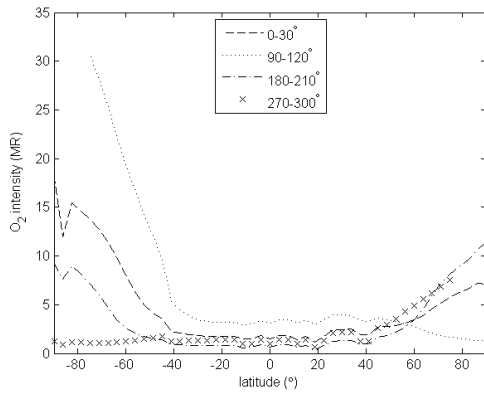
O₂ airglow



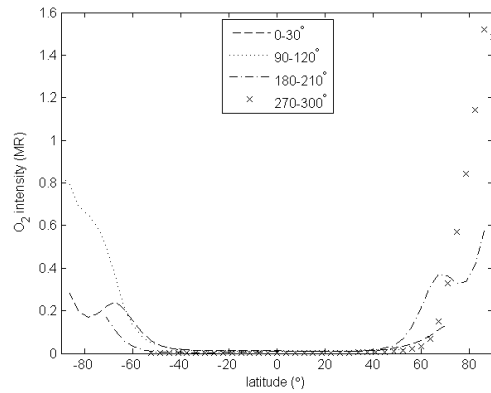
(a) case 1



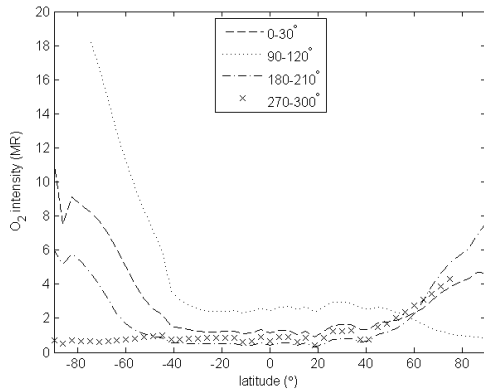
(a) case 1



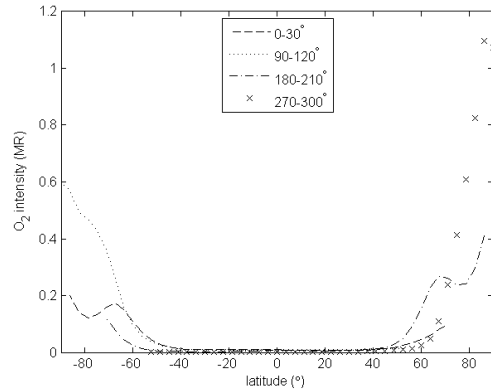
(b) case 2



(b) case 2



(c) case 3



(c) case 3

Figure 1: Simulated latitudinal variations of intensity from the O₂ IR Atmospheric band during daytime for different cases at different seasons L_S , as discussed in the text.

Figure 2: Simulated latitudinal variations of intensity from the O₂ IR Atmospheric band during nighttime for different cases at different seasons L_S , as discussed in the text.

REFERENCES

ing the three-body recombination reaction to match the intensity range observed. At night, we calculated that the brightest emission from the O_2 1.27- μm state would occur during the polar winters, with intensities above 1 MR over the North Pole.

We have shown that the daytime simulations are more sensitive to the CO_2 quenching rate while during the night, the simulations are more strongly affected by variations in the production yield. Our results therefore emphasize the need to properly quantify these two kinetic parameters to better reproduce the observed O_2 1.27- μm emission and to make reasonable predictions using different atmospheric conditions, e.g., high-dust periods. We are therefore looking forward to the publications of the results from both the SPICAM and MRO-MCS observations of the O_2 IR Atmospheric emission at night to compare our model results and validate our assumptions about the production yield and quenching rate by CO_2 of the $O_2(a^1\Delta_g)$ state in a CO_2 -dominated atmosphere.

References

- P. Connes, J. F. Noxon, W. A. Traub, and N. P. Carleton. $O_2(^1\delta)$ emission in the day and night airglow of Venus. *Astrophysical Journal*, 233(1):L29–L32, 1979.
- A. A. Fedorova, O. I. Korablev, S. Perrier, J. L. Bertaux, F. Lefèvre, A. Rodin, and A. Kiselev. Exploration of Mars in the SPICAM-IR experiment onboard the Mars-Express spacecraft: 2. Nadir observations: Simultaneous observations of water vapor and O_2 glow in the Martian atmosphere. *Cosmic Research*, 44(4):294–304, July 2006b.
- A. A. Fedorova, O. I. Korablev, S. Perrier, J.-L. Bertaux, F. Lefèvre, and A. Rodin. Observation of O_2 1.27 μm dayglow by SPICAM IR: Seasonal distribution for the first Martian year of Mars Express. *Journal of Geophysical Research-Planets*, 111(E9), 2006a.
- A. García Muñoz, F. P. Mills, T. G. Slanger, G. Piccioni, and P. Drossart. Visible and near-infrared nightglow of molecular oxygen in the atmosphere of Venus. *Journal of Geophysical Research-Planets*, 114, 2009. ISSN 0148-0227. doi: 10.1029/2009JE003447.
- B. Gondet, J.-P. Bibring, J.-L. Bertaux, and F. Montmessin. O_2 nightglow emission detection in the atmosphere of Mars, identified by the OMEGA/MEX investigation. volume 12. EGU General Assembly 2010, 2010.
- V. A. Krasnopolsky. Uniqueness of a solution of a steady-state photochemical problem - applications to Mars. *Journal of Geophysical Research-Planets*, 100(E2):3263–3276, February 1995.
- V. A. Krasnopolsky. Photochemistry of the martian atmosphere: Seasonal, latitudinal, and diurnal variations. *Icarus*, 185(1):153–170, November 2006.
- V. A. Krasnopolsky. Seasonal variations of photochemical tracers at low and middle latitudes on Mars: Observations and models. *Icarus*, 201(2):564–569, June 2009.
- V. A. Krasnopolsky. Venus night airglow: Ground-based detection of OH, observations of O_2 emissions, and photochemical model. *Icarus*, 207(1):17–27, May 2010.
- W. J. Lafferty, A. M. Solodov, C. L. Lugez, and G. T. Fraser. Rotational line strengths and self-pressure-broadening coefficients for the 1.27 μm , $a_g^{\Delta}-X^3\Sigma_g^-, v = 0 - 0$ band of O_2 . *Applied Optics*, 37(12):2264–2270, April 1998.
- D. McCleese and D. M. Kass. Results of the Mars climate investigations on the Mars Reconnaissance Orbiter. Number C31-0014-10, Bremen, Germany, 2010. 38th COSPAR Scientific Assembly 2010, COSPAR.
- J. F. Noxon, W. A. Traub, N. P. Carleton, and P. Connes. Detection of O_2 dayglow emissions from Mars and Martian ozone abundance. *Astrophysical Journal*, 207(3):1025–1035, 1976.
- S. Ohtsuki, N. Iwagami, H. Sagawa, Y. Kasaba, M. Ueno, and T. Imamura. Ground-based observation of the Venus 1.27 μm O_2 airglow. *Planetary Atmospheres, Ionospheres, and Magnetospheres*, 36(11):2038–2042, 2005.
- T. G. Slanger, T. E. Cravens, J. Crovisier, S. Miller, and D. F. Strobel. Photoemission phenomena in the solar system. *Space Science Reviews*, 139:267–310, 2008.