The ionospheric source of the red and green lines of atomic oxygen in the Venus nightglow

Jane L. Fox

Department of Physics, Wright State University, 3640 Colonel Glenn Hwy, Dayton, OH 45435, United States

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ABSTRACT

We have modeled the nightside ionosphere of Venus for 11 solar zenith angles between 90° and 165° with a view toward determining the intensities of the atomic oxygen red, green and 2972 Å features in the nightglow. The ionospheric source of these emissions is mainly dissociative recombination of O_2^+, which may proceed via four channels, which produce two O atoms in various combinations of the ground $O(^3P)$ state and the electronically excited $O(^1D)$ and $O(^1S)$ states. These excited states are the precursors to the nightglow features. We have modeled the $O_2^+(v)$ vibrational distribution for each of the models, and we have used it to determine branching ratios for the DR channels. We have assumed that the ionosphere is produced by transport of atomic ions from the dayside, and that the ratios of the atomic ions are the same as the model values of the upward ion fluxes on the dayside. For each model, we have normalized the downward atomic ion fluxes to the peak O^+ densities that were measured by the Pioneer Venus Orbiter Ion Mass Spectrometer. For the non-sunlit models, the O_2^+ densities peak in the altitude range 152–159 km. We have computed the density profiles of $O(^1D)$ and $O(^1S)$, and the integrated overhead intensities of the transitions for each of the models. We find that the average intensities, weighted by the area of the solar zenith angle bins, for the red, green and 2972 Å emissions are 26 R, 4.6 R, and 0.46 R, respectively. Thus the average high solar activity nightside ionosphere cannot produce green line intensities that are as large as the maximum intensity of about 150 R as measured from the ground. Our predicted red line intensities are, however, larger than the upper limits determined by ground based and spacecraft measurements. Possibilities for increasing the green line intensities and decreasing the red line intensities are discussed.

1. Introduction

The green line of atomic oxygen is a permanent feature of the terrestrial nightglow, and it was the first emission to be detected. It arises from a forbidden transition involving two of the lowest $2p^4$ metastable singlet states of atomic oxygen, $O(^1D)$ and $O(^1S)$. The transition

$$O(^1S_0) \rightarrow O(^1D_2) + hv, \tag{1}$$

produces the green line at 5577 Å; $O(^1S)$ may also emit to the $O(^3P)$ ground state

$$O(^1S_0) \rightarrow O(^3P_1) + hv, \tag{2}$$

producing the ultraviolet emission line at 2972 Å. The transition

$$O(^1D_2) \rightarrow O(^3P_{2,1}) + hv \tag{3}$$
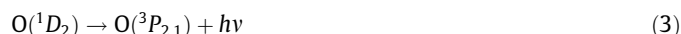
produces the red doublet at 6300, 6364 Å.

Efforts to detect the atomic oxygen red and green lines in the nightglow of Venus were first attempted more than 35 years ago. The visible spectrometers aboard the Soviet spacecraft Venera 9

and 10 recorded the 3000–8000 Å spectral region of the nightglow (e.g., Krasnopolsky et al., 1976). The investigators searched for the red and green lines but none were found. Upper limits of 20–25 R for the red line and 10 R for the green line were placed on their intensities (e.g., Krasnopolsky, 1986).

Several features were, however, detected by the Venera spectrometers including the $v' = 0$ progression of the Herzberg II $\left(c^1\Sigma_u^- \rightarrow X^3\Sigma_g^-\right)$ bands, which are characterized by more or less constant intensities. Also seen were the Herzberg I $\left(A^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-\right)$ bands, which are dominant in the terrestrial nightglow, the Chamberlain $(A'3\Delta_u \rightarrow a^1\Delta_g)$ bands, and the Slanger $(c^1\Sigma_u^- \rightarrow a^1\Delta_g)$ bands (e.g., Lawrence et al., 1977; Slanger and Black, 1978a; Krasnopolsky and Tomashova, 1980; Krasnopolsky, 1981, 1986). The ultimate source of these O_2 visible and infrared nightglow emissions is three-body recombination of O atoms that are produced on the dayside, mainly by the photolysis of CO_2:

$$CO_2 + hv \rightarrow CO + O. \tag{4}$$

The O atoms are transported upward and toward the nightside where they converge, flow downward and recombine to produce excited states of O_2:

E-mail address: jane.fox@wright.edu

$$O + O + M \rightarrow O_2^* + M. \tag{5}$$

Reaction (5) is exothermic by about 5.11 eV, so the excited O_2^* molecule may be any of the three Herzberg states, including $O_2\left(A^3\Sigma_u^+\right)$, $O_2(A'^3\Delta_u)$, $O_2(c^1\Sigma_u^-)$, the ground vibrational states of which lie 4.34, 4.25 and 4.05 eV, respectively, above the $O_2\left(X^3\Sigma_g^-; v = 0\right)$ ground state (Huber and Herzberg, 1979). Two lower energy states, $O_2\left(b^1\Sigma_g^+\right)$, and $O_2(a^1\Delta_g)$, the ground vibrational states of which lie 1.63 and 0.98 eV, respectively, above the ground state may also be formed, either initially by O atom recombination (Eq. (5)), by cascading from the higher excited states, or by excitation transfer.

The Visible and Infrared Thermal Imaging Spectrometer (VIRTIS) on board the European Venus Express (VEX) spacecraft has measured intensities of the Venus nightglow emissions in the wavelength range 0.3–5 μm since 2007, which until very recently was a period of very low solar activity. The VIRTIS instrument has revealed the presence of the Herzberg II and Chamberlain bands in the visible, but no evidence was found for the atomic oxygen green or red lines (e.g., García Muñoz et al., 2009).

On 20 November 1999, however, Slanger et al. (2001) aimed the Keck I telescope on Mauna Kea at the dark side of Venus. Using the HIRES spectrograph, they identified green line emission with an intensity of about 150 R. The emission was also detected in observations using the ARC Echelle Spectrograph (ARCES) at the Apache Point Observatory on 5 February 2001 and 16 December 2002 but its intensity was found to be lower than the initial detection by a factor of about three (Slanger et al., 2006). On 27 August 2002, the Keck HIRES spectrograph was aimed partially toward the Venus limb, and an intensity of 89 R was recorded. Currently, the green line has been detected a total of nine times (Gray et al., 2012). Other attempts to detect the green line on Venus from ground-based telescopes have yielded only upper limits to its intensity. One reason for the observed variability that has been suggested is that the original detection was at high solar activity, and marginal or non-detections have been at lower solar activity (Slanger et al., 2012).

In the terrestrial nightglow, $O(^1S)$ is assumed to be produced largely in the mesosphere by the so-called Barth (1961, 1964) mechanism. In this process, three body recombinations of O atoms produce O_2 in an electronically excited state (Eq. (5)). If the energy of the excited O_2^* molecule is greater than the excitation energy of the $O(^1S)$ state, about 4.19 eV, it may collide with and transfer its energy to an O atom
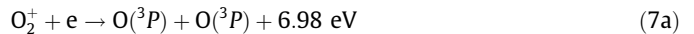
$$O_2^* + O \rightarrow O_2 + O(^1S), \tag{6}$$

producing $O(^1S)$. The excited state O_2^* in the Barth mechanism has not been identified, although several suggestions have been put forth, including the A, A', and c states in high vibrational levels, or the weakly bound $^5\Pi_g$ state (e.g., Smith, 1984; Krasnopolsky, 1986). An excellent review of the O_2 excited states and their emissions in both the laboratory and the atmosphere has been presented by Slanger and Copeland (2003).

On Earth the major emission in the visible O_2 nightglow is the Herzberg I band system, which originates from the $O_2(A–X)$ transition. On Venus, however, the major O_2 visible emission features are the Herzberg II bands, which are formed by the $O_2(c–X)$ transition. The $O_2(c)$ state is efficiently vibrationally quenched by CO_2, and the $v = 0$ state does not have enough energy to produce $O(^1S)$ in reaction (6). Slanger et al. (2012) have put forward arguments that the $O(^1S)$ atoms, if produced by the Barth mechanism, are formed at higher gas densities than their terrestrial counterparts, where the emission efficiency is smaller. They suggest that the observed green line therefore does not arise from the mesospheric source,

but from higher altitudes, which places it in the ionosphere. On Earth this source of $O(^1S)$ is known as the "F-region" component, and it is comparatively weak (e.g., Liu et al., 2008).

The ionospheric source of $O(^1S)$ atoms mainly results from dissociative recombination (DR) of O_2^+, which may proceed via the following four channels:

$$O_2^+ + e \rightarrow O(^3P) + O(^3P) + 6.98 \text{ eV} \tag{7a}$$
$$\rightarrow O(^1D) + O(^3P) + 5.02 \text{ eV} \tag{7b}$$
$$\rightarrow O(^1D) + O(^1D) + 3.05 \text{ eV} \tag{7c}$$
$$\rightarrow O(^1D) + O(^1S) + 0.83 \text{ eV}. \tag{7d}$$

The exothermicities listed above are for O_2^+ molecules in the ground vibrational state, and the internal energies of the O_2^+ must be added to the exothermicities. Although it is exothermic by 2.79 eV, the branching ratio for the channel that produces $O(^1S) + O(^3P)$ has be shown to be effectively zero, and the production of $O(^1S)$ therefore arises only from channel (7d).

The formation rates of $O(^1D)$ and $O(^1S)$ in DR depend therefore on the values of the DR coefficient, and on the branching ratios for the channels (7a)–(7d). DR of O_2^+ is one of the most studied reactions, both experimentally and theoretically. Although in many experiments the vibrational distribution of $O_2^+(v)$ is unknown, the DR coefficient has been found not to vary substantially from one measurement to another. In fact, the DR coefficient of O_2^+ is sometimes measured to verify the normalization of the apparatus (e.g., McLain et al., 2004). Its value at thermal energies is about 2×10^{-7} cm^3 s^{-1} to within about 10%, and the electron temperature dependence at low temperatures is about $T_e^{-0.7}$. There is some evidence, however, that the total DR coefficient decreases slightly with increasing vibrational level (Petrignani et al., 2005a), but there is no quantitative data available that would allow the incorporation of this effect into models. As a first approximation, we have adopted the total DR rate coefficient of Mehr and Biondi (1969): $1.95 \times 10^{-7} \ (300/T_e)^{0.7}$ cm^3 s^{-1} for T_e less than 1200 K; and $7.39 \times 10^{-8} \ (1200/T_e)^{0.56}$ cm^3 s^{-1} for T_e greater than 1200 K, and we do not vary it with vibrational level. In regions where DR is the main loss mechanism for O_2^+, use of a smaller or larger DR coefficient would result in O_2^+ densities that increase or decrease, respectively, to compensate for the change in the DR coefficient. Thus to first order the total rate of DR would not change appreciably.

Although the Venus nightside thermosphere is characterized by low neutral temperatures, the relevant temperatures for DR are the electron temperatures, T_e. The electron temperatures in the Venus nightside ionosphere at high solar activity have been measured by the Pioneer Venus (PV) Orbiter Langmuir Probe (OETP) and by the retarding potential analyzer (ORPA), and have been found not to vary much over the nightside (e.g., Miller et al., 1980). At low altitudes we expect the values of T_e to be thermalized with the neutral temperatures, but they may reach values of up to about 3000 K at 250 km, and about 5000 K near 800 km (e.g., Bauer et al., 1985).

The branching ratios for the four channels of O_2^+ DR (7a)–(7d), however, have been found to depend on both the collision energy and on the vibrational level of the ion. The branching ratios have been measured in ion storage rings as a function of collision energy for vibrationally relaxed $O_2^+(v = 0)$ by Peverall et al. (2001), who reported branching ratios at 10 collision energies from 0 to 300 meV, and by Petrignani et al. (2005b), who measured the branching ratios at 13 energies from 1 meV to 281 meV. Their results in general are not in good agreement with each other, and for the most part do not show smooth trends. Petrignani et al. (2005b) found that the branching ratio for channel (7a), which is the most exoergic channel, is between 0.22 and 0.33 for all the energies, and seems to vary if not monotonically at least