Discovery of the Atomic Oxygen Green Line in the Venus Night Airglow

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Green line emission at 557.7 nanometers arising from the $O(^1S - {}^1D)$ transition of atomic oxygen has been observed on the nightside of Venus with HIRES, the echelle spectrograph on the W. M. Keck I 10-meter telescope. We also observe optical emissions of molecular oxygen, consistent with the spectra from the Venera orbiters, but our green line intensity is so high that we cannot explain how it could be inconspicuous in the Venera spectra. An upper limit for the intensity of the $O(^1D - {}^3P)$ oxygen red line at 630 nanometers has also been obtained. The large green/red ratio indicates that the source is not associated with the Venus ionosphere. An important conclusion is that observation of the green line in a planetary atmosphere is not an indicator of an atmosphere rich in molecular oxygen.

Optical emissions from planetary atmospheres provide information about atmospheric composition, energy deposition from solar radiation and the solar wind, atmospheric dynamics, coupling with planetary magnetic fields, and chemical relaxation processes after excitation. Dayside solar illumination of the upper atmospheres of Earth, Venus, and Mars produces intense emission called dayglow (*1–3*). In addition, a fraction of the ambient molecular constituents are ionized or dissociated into atoms. Nightside recombination of atoms with each other or of ions with electrons produces electronically excited molecules whose emissions are called nightglow. Here, we concentrate on nightglow from Venus and compare it with nightglow from Earth.

The atmospheric parameters of the two planets are quite different. Whereas the terrestrial atmosphere is primarily composed of O_2 and N_2, the venusian atmosphere consists largely of CO_2, with a 5% admixture of N_2. In addition to the far hotter temperature at the venusian surface, the surface pressure on Venus is about 100 atmospheres.

The principal emitter in the ultraviolet from Earth's nightglow is molecular oxygen, whereas the near-infrared is dominated by the Meinel bands of the hydroxyl radical, OH. Oxygen molecules absorb solar radiation on the dayside at wavelengths shorter than 240 nm and dissociate. At altitudes of about 95 km, the resultant oxygen atoms recombine with each other to produce excited oxygen molecules in a variety of excited states

$$O(^3P) + O(^3P) + M \rightarrow O_2^* + M \quad (1)$$

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where M is a third body, and O_2^* represents any of the six bound states of O_2 that are commonly considered, $O_2(A, A', c, b, a, X)$. Nightglow emissions from excited oxygen atoms result from energy transfer

$$O_2^* + O(^3P) \rightarrow O_2 + O(^1S) \rightarrow 557.7 \text{ nm} \quad (2)$$

or electron-ion recombination (at much higher altitude)

$$O^+ + e \rightarrow O(^1S, {}^1D) + O(^3P) \rightarrow 557.7, 630.0 \text{ nm} \quad (3)$$

$$O^+ + e \rightarrow O(^{3,5}P) \rightarrow 844.7, 777.4 \text{ nm} \quad (4)$$

The nightglows of Earth and Venus both contain strong molecular oxygen emissions, but the appearance of the spectra and the inferences about atmospheric chemistry that can be based on them are different. On Venus a single vibrational level (v = 0) of a single electronic state, $O_2(c)$, produces more than 80% of the emissions in the visible region (*4*). On Earth, a wide range of excited vibrational levels from three electronic states, $O_2(A, A', c)$, are observed (*5, 6*) primarily in the ultraviolet region, whereas the strongest single feature in the visible region is the oxygen green line.

Here, we report the first ground-based measurements of the visible nightglow spectrum of Venus with high spectral and spatial resolution. The original objectives of our observations of the venusian nightglow were to verify the visible emissions from molecular oxygen observed by the Russian Venera orbiters (*4*) and to use the superior spectral resolution of HIRES to search for weaker molecular emissions from other electronic states and excited vibrational levels. In so doing, we found relatively intense emission from the oxygen green line at 557.7 nm, in direct contrast to the results of the Venera observations.

Venus was observed with HIRES at 1600 UT on 20 November 1999. The planet was acquired at a fixed sky position angle to orient a 7-arcsec-long by 0.86-arcsec-wide slit perpendicular to the anti-solar (nightside) limb. The observed emission is a composite of narrow source emission lines, an underlying planetary reflectance continuum, and terrestrial sky continuum and emission. The exposure times varied from 100 to 500 s, with closed-loop guiding on Venus. The results reported here were obtained in clear sky conditions, with good seeing (1.2″) in moderate air mass (1.33). The spectral resolution was 37,000; the relative planetary velocity was 12.8 km/s.

The sequence of stacked spectra (Fig. 1) shows the terrestrial green line and the red-shifted venusian green line, going from the bottom on the interior of the planetary disc toward the limb at the top. The spectra are separated by 0.19 arcsec and averaged over 1 arcsec. The terrestrial intensity stays constant, as does the venusian intensity until the limb is approached. Then, the venusian intensity approximately doubles, decreasing as the line-of-sight goes off the planet. Each of these spectra is a difference spectrum, where the appropriately scaled solar-illuminated spectrum is subtracted from the darkside spectrum. The limb crossing occurs near 1.5 arcsec on the *y* axis.

The inset to Fig. 1 shows a set of spectra for the 630-nm red line. The terrestrial red line is strong, and there is a weak feature to the long-wavelength side at the correct position of the venusian red line. However, it is at the noise level, and does not brighten toward the limb. The red line spectra are aligned with the green line spatial positions, i.e., at 0.57, 1.14, and 1.71 arcsec. We use the deduced limb intensity to set an upper limit on the strength of the venusian red line.

The photon counts received by the HIRES charge-coupled device (CCD) detector were analyzed to determine the absolute intensities of the venusian and terrestrial emissions. The venusian green line intensity varies from 440 rayleighs near the terminator to 830 R at the tangent point (limb), along the slant observation path. The terrestrial intensities are 470 R for the green line and 1.3 kR for the red line. The terrestrial and venusian irradiances were corrected for the telescope and instrument efficiency, apparent slit width, and detector gain. The venusian data are additionally corrected for terrestrial atmospheric absorption. When the terrestrial intensities are referenced to the zenith (Venus was 39.3° above the horizon), the measured brightnesses become 300 and 830 R for the terrestrial green and red lines, respectively (*7*).

As observed from Earth, emissions from the atmosphere of Venus are brighter than would be calculated from the volumetric emission rate. Of primary importance is that the dense clouds on Venus below the airglow layer have a very high albedo, scattering downward-propagating radiation back to space. Because of the nature of scattering by the diffuse clouds, the overall effect is that signals seen from Earth are about three times larger than the Venus zenith intensity (*8*). In addition, the increasing length of the slant path as the viewpoint is scanned toward the limb results in an increasing intensity (Fig. 1). Our estimate of the vertical green line intensity, away from the limb, is 150 R, with an estimated error of ±20%. Little variability is apparent in the venusian green line intensity in the spectra of Fig. 1, at least on the scale of the spatial resolution, which is about 600 km. The estimated upper limit on the Venus vertical red line intensity is 20 R.

In the 551- to 552-nm region we expect to find rotational lines from the strong 0-10 Herzberg II band, the electronic transition from the $O_2(c)$ state to the $O_2(X)$ ground state. Shown at the top of Fig. 2 are the traces of the barely differentiable (scaled) dayside and nightside spectra. When the difference between the two is amplified and compared with a spectrum that simulates the Herzberg II 0-10 band, we see that a majority of the 14 lines appearing in the simulation are discernible in the venusian difference spectrum (*9*). There are some distortions in the data due to the solar Fraunhofer lines, from light scattered into the telescope from the venusian dayside. For instance, the strong Fraunhofer line at 551.3 nm appears as a distortion in the difference spectrum.

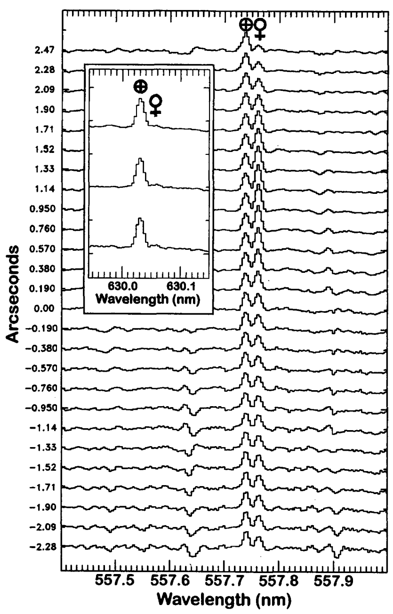

Fig. 1. Keck/HIRES spectra near the regions of the O(^{1}S − ^{1}D) green line and the O(^{1}D − ^{3}P) red line. Stacked 557 to 558 nm spectra from interior of Venus disc at bottom to limb at top, obtained in 8 min of observation. The terrestrial green line at 557.7 nm remains constant, but the red-shifted Venus green line becomes stronger as the limb is approached. The spectra are presented in 0.19-arcsec (115 km on Venus) steps, and averaged over 1 arcsec. The inset shows the terrestrial and venusian oxygen red lines, and the spectra are aligned with the equivalent green line spectra.

Summing the intensities of the O_2 lines appearing in the middle spectrum of Fig. 2 and calibrating against the 150-R green line, we find an intensity of about 270 R. At 200 K, the measured lines represent 37% of the entire $O_2(c\text{-}X)$ 0-10 band, which thus has an intensity of 720 R. Using known transition probabilities (*10*), the Herzberg II 0-10 band represents 14% of the emission for the entire v′ = 0 progression, leading to a value of 5.1 kR for that progression in the Herzberg II system.

Dispersed venusian nightglow was first observed in 1975 by the Venera 9 and 10 orbiters (*4*). Strong emissions were assigned to the Herzberg II bands of molecular oxygen, from v′ = 0 (*11*). Later analysis showed the presence of the O_2 Chamberlain bands, emissions from the $O_2(A')$ state (in v′ = 0) to the $O_2(a)$ state (*12*). No emissions from O(^{1}S) at 557.7 nm or O(^{1}D) at 630.0 nm were evident. Contemporaneous ground-based telescope observations in the infrared at about 1270 nm showed intense emissions from $O_2(a)$ to the ground state (*13*). Later observations by the Pioneer Venus Orbiter demonstrated that in the ultraviolet (155 to 360 nm), the venusian nightglow contains no evidence of molecular oxygen emissions and is instead dominated by emissions of nitric oxide from N + O recombination (*14–17*). The venusian nightglow, from the ultraviolet to the infrared, reflects the chemistry of minor atmospheric species rather than the main atmospheric component, carbon dioxide.

The 5.1 kR of Herzberg II O_2 emission observed here may be compared with 2.7 kR measured by (*4*) and 4 to 6 kR measured by the Pioneer Venus star tracker over the unresolved 400- to 800-nm range (*18*). Thus, it seems that the O_2 Herzberg II emission intensity, averaged over the disc, is fairly constant in the venusian nightglow. The lower intensity of the Venera observations is probably attributable to the timing of their recording, close to the minimum of the solar cycle, whereas the Pioneer-Venus and the observations here were carried out near solar maximum.

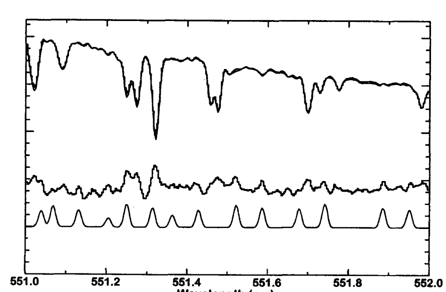

Fig. 2. Venus spectrum from 551 to 552 nm. (Top) Dayside and nightside spectra, normalized for best coincidence on the Fraunhofer lines; (middle) the day/night difference spectrum from Keck/HIRES; (bottom) 200 K simulation of a portion of the $O_2(c\text{-}X)$ 0-10 band.

However, the present observation of 150 R of green line emission is very different from what was reported from Venera 9/10 (*4*). Krasnopolsky set upper limits on the Venus green line intensity of 5 R (*19*) and 10 R (*20*). We compare the appearance of the Venera O_2 Herzberg II 0-10 band region (*4*) with a simulation based on degrading the 0.017-nm spectral resolution of HIRES to the Venera value of 2.5 nm (Fig. 3). The components of the simulation consist of 720 R of O_2 Herzberg II 0-10 band emission and 120 R of O_2 Chamberlain 0-6 band emission, both calculated at 200 K, and 150 R of green line. The green line is evident in the composite simulation but not in the Venera data. Considering that the O_2 emissions have remained relatively constant, it is puzzling that the green line emission is so variable. Current models of the nightside chemistry of the Venus atmosphere near an altitude of 100 km have taken the lack of green line emission as a key calibration point in understanding the differences between the atmospheres of Venus and Earth.

It has been suggested that the green line is an atmospheric diagnostic suitable for detecting the presence of O_2 in atmospheres of extrasolar planets (*21*). The present observations show that the green line intensities in the nightglows

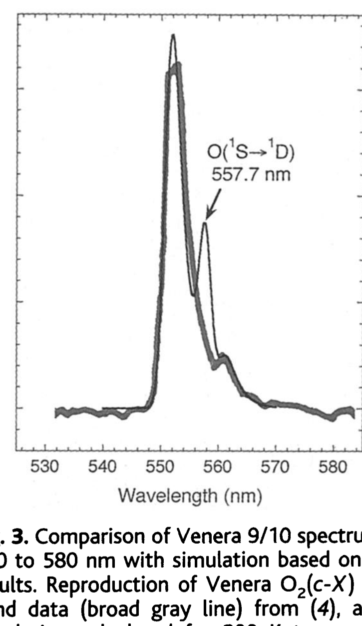

Fig. 3. Comparison of Venera 9/10 spectrum at 540 to 580 nm with simulation based on new results. Reproduction of Venera $O_2(c\text{-}X)$ 0-10 band data (broad gray line) from (*4*), and a simulation calculated for 200 K temperature and 2.5-nm resolution (narrow black line), constructed from 720 R of the $O_2(c\text{-}X)$ 0-10 band, 120 R of the $O_2(A'\text{-}a)$ 0-6 band, and a 150 R green line.

of Earth and Venus are quantitatively similar, even though the terrestrial and venusian atmospheric compositions are quite different. Although the green line intensity is potentially a measure of oxygen atom densities in planetary atmospheres, the present measurement demonstrates that green line production is not limited to planets with an Earth-like atmosphere.

The high venusian green/red line intensity ratio leads to the conclusion that the green line originates in the atom recombination region, rather than in the ionosphere. Ionospheric production strongly favors the red line, and Fox (*22*) predicts 46 R of red line emission from the Venus ionosphere but only 1 to 2 R of green line. Because the venusian atomic oxygen 630-nm red line intensity is no more than 10 to 15% that of the green line, we conclude that the $O(^1S)$ is being produced via Eqs. 1 and 2 near 100-km altitude, not via Eq. 3.

The identity of the O_2^* intermediate is controversial (*23*, *24*), although in recent years $O_2(c)$ has been favored (*25*), although among the three Herzberg states generated in the terrestrial atmosphere $O_2(c)$ emission is the weakest (*5*, *6*). In the venusian atmosphere, the situation is reversed and the $O_2(c)$ emission is the strongest (*4*), but the single vibrational level observed has insufficient energy to generate the green line by Eq. 2. Since the Venera missions, these two facts appeared to support each other. Now the mechanisms must be reconsidered.

The other O_2 emitter identified in the Venus visible spectrum thus far, the v = 0 level of the $O_2(A')$ state (*12*), has 0.08 eV more energy than needed to generate the green line via Eq. 2. The total intensity of its v′ = 0 progression (based on 120 R in the Chamberlain 0-6 band) is 700 R, i.e., somewhat more than all the emission from the Herzberg states in the terrestrial atmosphere (*5*, *6*). We also note that if venusian emission from $O_2(c, v \geq 2)$, suspected of being the transfer agent in the terrestrial atmosphere, had the same intensity as on Earth [about 100 R (*5*)] it would be indiscernible in the Keck/HIRES or the Venera spectra because it would be spread among many bands and rotational levels.

Lastly, it is important to point out that despite the O_2 Herzberg II band emission and the far more intense O_2 Infrared Atmospheric band emission at 1.27 μm (*8*), ground-state O_2 is reactively destroyed in the Venus environment (*26*). Absorption measurements using scattered solar light from the dayside reveal an upper limit on the O_2 mixing ratio between 10^{-6} and 10^{-7} (*27*).

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7. The terrestrial green line intensity is rather high for the tropical nightglow (*28*), but because the measurements were made only 20 min before sunrise there is a large dayglow component. The solar depression angle of only 5° corresponds to a shadow height of 25 km, so the ionosphere is well illuminated and both the green and red lines are strong, with an intensity ratio I(630)/I(557.7) of about 3. In the nightglow, this ratio is considerably less than unity, approaching zero as the ionospherically produced $O(^1D)$ decays away, whereas the $O(^1S)$ concentration only falls to the level determined by its generation in the ~95-km atom recombination region.
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Birth of the Kaapvaal Tectosphere 3.08 Billion Years Ago

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The crustal remnants of Earth's Archean continents have been shielded from mantle convection by thick roots of ancient mantle lithosphere. The precise time of crust-root coupling (tectosphere birth) is poorly known but is needed to test competing theories of continental plate genesis. Our mapping and geochronology of an impact-generated section through the Mesoarchean crust of the Kaapvaal craton indicates tectosphere birth at 3.08 ± 0.01 billion years ago, roughly 0.12 billion years after crust assembly. Growth of the southern African mantle root by subduction processes occurred within about 0.2 billion years. The assembly of crust before mantle may be common to the tectosphere.

As one of Earth's oldest surviving fragments of continental lithosphere, the Kaapvaal craton is a valuable archive for understanding the processes that generated the Archean continents. The crystallization ages of the Kaapvaal crust range from 3.6 to 2.6 billion years ago (Ga) [(*1*) and references therein] and its mantle root is as old as 3.5 billion years (Gy) (*2*); however, the time at which the crust and mantle became physically coupled to form a thick (150 to 300 km), stable continental plate [i.e., tectosphere (*3*)] is poorly known. At issue for all tectosphere is whether the conjoined mantle root and crust formed together (*4*) or separately (*3*, *5*). The age of Kaapvaal tectosphere formation was estimated to be at least 3.3 ± 0.2 Ga, based on Sm-Nd ages from mineral inclusions in diamond (*6*) and on evidence for crustal assembly of its Mesoarchean nucleus by 3.2 Ga (*7*). A craton-wide overprinting episode of granitoid magmatism at 3.1 Ga was attributed to "intracrustal melting" after a 3.2 Ga orog-

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