Ozone: Twilit Skies, and (Exo-)planet Transits

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Although only a trace constituent gas in the Earth's atmosphere, ozone plays a critical role in protecting the Earth's surface from receiving a damaging flux of solar ultraviolet radiation. What is not generally appreciated, however, is that the intrinsically weak, visible Chappuis absorption band becomes an important influence on the colour of the entire sky when the Sun is low or just below the horizon. This effect has been explored using spectra of the sunset and also of the eclipsed Moon; phenomena that involve a similar passage of sunlight tangential to the Earth's surface. This geometry will also be relevant in future attempts to perform transit spectroscopy of exo-Earths.

Introduction

The colours seen by an observer of the Earth's sky, from within or from without the atmosphere, can be rich and varied. The processes that result in this palette are geometrically complex, but comprise a limited number of now well-understood physical effects. This understanding was not gained easily. From the time when early humans first consciously posed the question: *"What makes the sky blue?"*, to the time when the processes of scattering by molecules and molecular density fluctuations were elucidated, thousands of years passed, during which increasingly intensive experiments and theories were developed and carried out (Pesic, 2005).

Most physicists, if asked why the sky is blue, would answer with little hesitation: *"Because of Rayleigh scattering by molecules."* With the Sun above the horizon in a clear sky, this is worth a good mark. During twilight, however, things get more complicated.

Twilight has a special place in the life of an observational (optical/near-infrared) astronomer who is privileged to witness it from some of the most spectacular sites on the planet. The geometry of the illumination of the atmosphere at twilight is also very pertinent to the study of transiting exoplanets, when the path of starlight is tangential to the planetary sphere.

This article is about the effect of ozone on the colour of the twilit sky and, in the same vein, its appearance as the strongest telluric absorption feature in the visible spectrum of the Earth as it would be seen by a distant observer watching it transit in front of the Sun. We present and analyse spectrophotometric observations of sunset and also discuss observations of the eclipsed Moon reported by Pallé et al. (2009).

Ozone

Ozone (O_3 or trioxygen) is an unstable allotrope of oxygen that most people can detect by smell at concentrations as low as 0.01 parts per million (ppm). When present in the low atmosphere as a pollutant, it has many damaging effects, including to lung tissue. At higher altitudes, typically between 15 and 40 km, however, it produces the beneficial effect of preventing damaging ultraviolet (UV) radiation from reaching ground level. The Hartley band, extending between 200 and 300 nm, absorbs very strongly in this region with a maximum at 255 nm. The UV absorption extends, more weakly, in the Huggins band up to around 360 nm. In the visible spectrum, a radial path through the atmosphere exhibits very little ozone absorption but, as the column increases at greater zenith distances, the Chappuis band begins to have an appreciable effect by absorbing across the entire visible spectrum with a maximum close to 600 nm. More absorptions, in the Wulf bands, appear in the infrared at 4.7, 9.6 and 14.1 μm.

By absorbing red and orange light, the Chappuis band has the effect of imparting a pale blue colour to pure ozone gas in the laboratory. As the Sun approaches the horizon, the increasing optical depth in the Chappuis band begins to have an effect on the sky colour that, at twilight, dominates the effect due to Rayleigh scattering (Hulbert, 1953). The colour of the clear zenith sky as the Sun

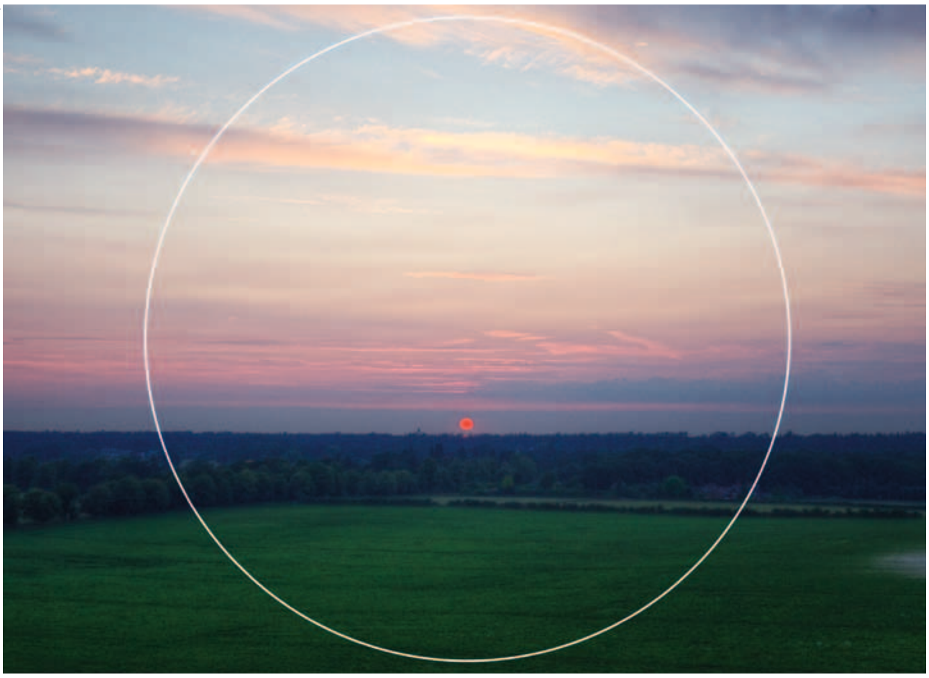

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Figure 1. A few minutes before sunset at the Appleton Water Tower in Norfolk on 27 June 2010. The white circle shows the approximate pointing and acceptance aperture of the fibre input to the spectrometer. The deep red Sun and the haze at the horizon suggest a high atmospheric aerosol content which is reflected in the model fit to the spectrum.

sets is far bluer than can ever be achieved by Rayleigh scattering alone and simple models demonstrate that, in the absence of ozone, it would be a pale grey–yellow shade at this time. Observations of the sky and/or the setting sun with a spectrometer show what a profound effect the ozone has on the telluric spectrum, as it far exceeds the effects produced by water and diatomic oxygen absorption (so familiar to optical spectroscopists) on the visible spectral energy distribution.

Spectral measurements and models

We have made a series of specrophotometric measurements of both the sky and the Sun, covering a period from several hours before sunset up to a short period afterwards. These have been made under both clear and overcast skies using a fibre input to a spectrometer, which results in an effective input aperture with a full width half maximum (FWHM) of 25°. The spectrometer, an Ocean Optics Jaz, covers a wavelength range of 350–1000 nm in 2048 spectral channels with a spectral resolution of 1.5 nm (FWHM). Exposure times range from 3 to over 100 ms per integration with each observation being the average of 32 or 64 individual exposures.

Sunset

Reported here are data collected from the top of a tower (the Appleton Water Tower[1]) in Sandringham, Norfolk, England on the evening of the 27 June 2010 with the axis of the input fibre tracking the position of the Sun to within a few degrees. The scene just preceding sunset is shown in Figure 1, where it can be seen that the sky is partially cloudy and quite hazy on the horizon, suggesting a relatively high atmospheric aerosol concentration. With our large angular input aperture, and especially at the shorter wavelengths, the scattered light from the sky becomes the major contributor to the signal when the Sun is below a few degrees in altitude.

Figures 2a and 2b show a spectrum (black line) constructed as an average of four observations taken during the half hour before sunset. In order to remove the Fraunhofer lines originating in the solar atmosphere, the observed spectrum is divided by one taken five hours before sunset. This shows the very strong telluric water and diatomic oxygen absorptions expected at large zenith distances. It also shows the very broad dip, centred at about 585 nm, due to the Chappuis band of ozone. Note the coincidence of a pair of water bands with the central structure of the ozone Chappuis absorption between 560 and 600 nm. This ozone feature is prominent in the spectrum of sunset viewed with a visual spectroscope.

In order to model the overall shape of this spectrum we have used an analytic representation of molecular Rayleigh scattering, taken from Allen (1973), expressed per atmo-cm (thickness of atmospheric layer in cm when reduced to standard temperature and pressure, STP). This gives a scattering cross-section which varies as wavelength to the power −4.05 to take account of the scattering and the wavelength variation of refractive index. It is normalised to give an optical depth of 0.098/atmo-cm at 550 nm. For dust and aerosols, we use Allen's wavelength exponent of −1.3, normalised to give an optical depth of 0.195/atmo-cm at 550 nm, which corresponds to normally clear conditions. For the ozone cross-section we use data from the project Spectroscopy & Molecular Properties of Ozone[2], normalised to give an optical depth of 0.0268 at 550 nm for 0.3 atmo-cm (taken as the standard ozone depth).

We consider two types of atmospheric path to compute the spectrum ratios relative to the high Sun. The first is the direct line of sight to the Sun, where we account for Rayleigh and aerosol scattering out of the beam and ozone absorption. The optical depth is derived from the atmospheric path as a function of solar zenith distance, choosing scaling factors of order unity for the aerosol and ozone contributions relative to the Rayleigh scattering.

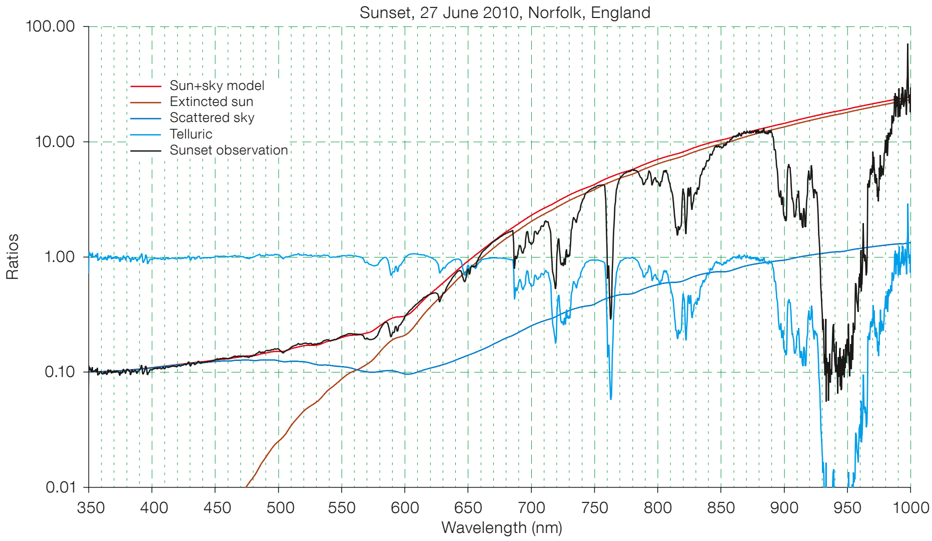
The second contributor is scattered skylight summed from a set of twelve equal logarithmically-spaced atmospheric paths up to 100 atmo-cm. Each path is given a weighting factor chosen to match the spectral shape. The initial values were chosen based on the geometry of the observation, but then adjusted to give the best match. The aerosol and ozone scaling factors can be chosen independently from those applied to the direct solar path. Each sky path has a source term that is proportional to the sum of the Rayleigh and aerosol cross-sections and a negative exponential sink term that represents ozone absorption and molecular and aerosol scattering out of the beam, both scaled for pathlength. Finally, the relative contributions of direct sunlight and skylight are adjusted to take account of the balance imposed by the large input aperture.

Although this model serves the purpose of a rather complicated fitting function, rather than an *ab initio* calculation, it does give a very good feel for how the skylight we see is influenced by the geometry it has to negotiate on its path through the atmosphere. We stress that the complexity derives from the geometry rather than the physics of absorption and scattering.

Figure 2 (upper) shows the separate components of direct sunlight (brown line) and the combination of a set of different paths involving a single scattering from the sky (dark blue line). The combination of the two is shown as a red line, and the ratio of the data to the model gives a normalised telluric spectrum containing the O_2 and H_2O features that we do not model (light blue line). Figure 2 (lower) shows the same model except for the ozone contribution that is set to zero for both the direct and the scattered paths.

Lunar eclipse

The deep, copper-coloured illumination of the eclipsed Moon represents the extinction and forward scattering of the Sun's light by a tangential passage through the Earth's atmosphere summed over the entire range of altitudes where the optical depth is significant (see Figure 3 for a sequence of photographs of the 2010 winter solstice lunar eclipse). This geometry is similar to that which applies when a transiting planet is seen against the disc of its parent star. This



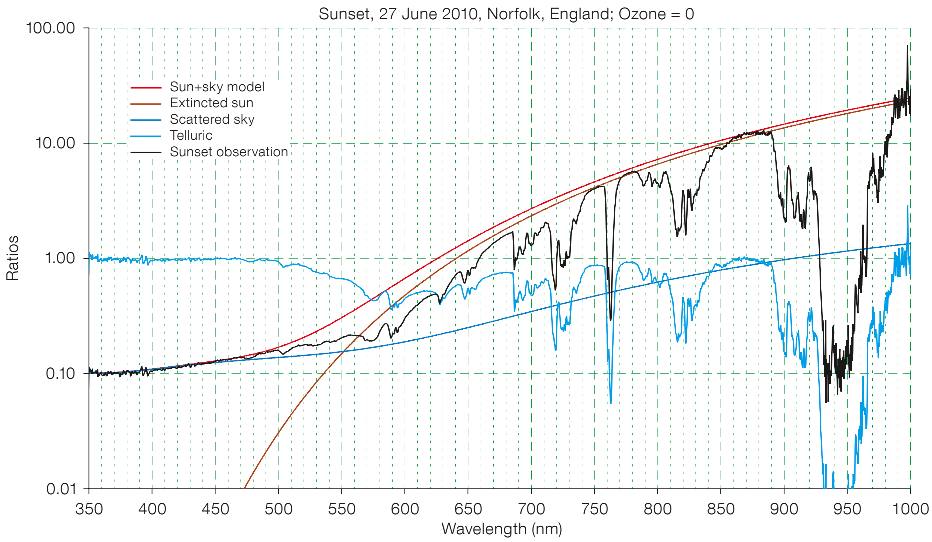


Figure 2. Upper: The visible and near infrared spectrum of the setting Sun (black line). The red line shows our model fit to this observed ratio, comprising the addition of the direct extincted light from the Sun (brown line) and the combination of a set of different paths involving a single scattering from the sky (dark blue line). The light blue line shows the ratio of the observed spectrum to the model fit and so reveals the telluric absorption due to diatomic molecular oxygen and water vapour. Lower: The same model fit but with the ozone content of the atmosphere set to zero. This gives a good idea of the extent of the ozone effect on the spectrum when the Sun is at large zenith distances.

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Figure 3. A photo-montage of the Moon during the eclipse coinciding with the 2010 winter solstice on 21 December. This gives an excellent representation of the orange/copper colour of the illumination within the umbra of the Earth.

recognition prompted Pallé et al. (2009) to make the first comprehensive optical/infrared observations of an eclipsed Moon with modern, digital spectrophotometers. Using a combination of measurements of the uneclipsed Moon and the penumbra and umbra during the eclipse, they were able to cancel the solar spectral features (Fraunhofer lines) and the effects of the lunar albedo and also to minimise the effect of variations in the telluric spectrum caused by the path from the telescope to the Moon during the observations.

Within the umbra of the Earth's shadow, the residual illumination is produced by refracted and forward-scattered sunlight passing almost tangentially through all levels of the Earth's atmosphere. The integral of these paths is complex and depends on the distribution of clouds in the troposphere and above. The penumbra, as seen from the Moon, is analogous to sunset, with contributions both from direct sunlight and scattered skylight.

We have taken the visible and near-infrared eclipse spectrum from Pallé et al. and performed a fit to it using a model similar to the one we used for the sunset spectrum. We assume that, in the visible, the umbral spectrum does not contain a significant contribution from direct sunlight, so we have restricted our fitting to the use of multiple scattering paths from the sky. Figure 4 shows the result of this fitting, both with and without the contribution of ozone. The ability of the ozone model to match the small wiggles in the spectrum, especially around 500 nm, is to be noted.

A good physical insight into the formation of this spectrum is obtained by looking at examples of sunset and sunrise seen from Earth orbit. Astronauts on the International Space Station have obtained many such images and we have chosen one of them for Figure 5. This shows the illuminating source as it would appear at the boundary between the umbra and penumbra of an eclipse. There are several things to note in this image. At low altitudes there is strong but highly reddened forward scattering. This produces the steeply rising spectrum longward of 600 nm. At high altitudes, there is a large solid angular contribution from optically thin Rayleigh scattering that is responsible

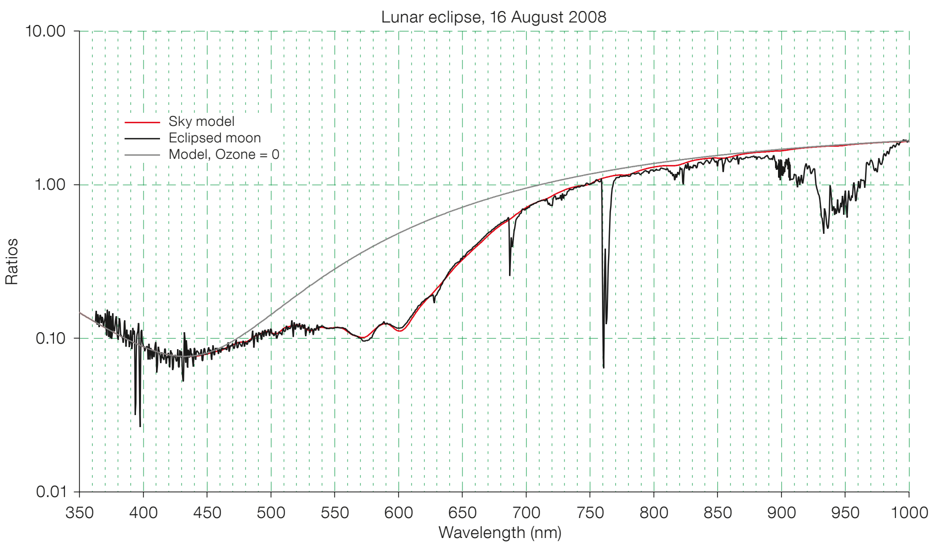

Figure 4. The visible and near-infrared part of the spectrum of the August 2008 lunar eclipse (black line) published by Pallé et al. (2009). This is the ratio of the umbral to the penumbral spectrum taken at the same average airmass, resulting in the removal of the solar and lunar spectral signatures as well as minimising the telluric features resulting from the path between the telescope and the Moon. The red line shows our model fit to the data. The smooth grey line is the same model without ozone absorption. The sharp upturn in the blue is due to pure, unabsorbed Rayleigh scattering contributed by the very outer regions of the Earth's atmosphere illuminating the eclipsed Moon.

NASA

Figure 5. An image of a sliver of direct sunlight photographed from the International Space Station [ISS015-E-10471, 3 June 2007, courtesy of NASA]. This illustrates the colour of the light source that illuminates the eclipsed Moon at the boundary between the umbra and penumbra of the Earth's shadow (see Figure 4). We note that the darker, dirty yellow band dividing the troposphere from the stratosphere corresponds to the region of maximum ozone absorption and so demonstrates that the Chappuis band is visible without the use of a spectrometer!

for the spectral rise shortward of 420 nm. We do not see this latter effect so strongly from the surface of the Earth at sunset because there is no path to the Sun with a length of less than an atmo-cm (except at high altitude of course). Perhaps the most remarkable feature of the image, however, is the presence of the dark, dirty-yellow band just above the clouds at the troposphere/stratosphere boundary. We propose that this is the visible representation of the Chappuis ozone absorption at heights above 15 km. In other words, the vertical sequence of horizontal bands of colour in the image of sunset/rise map directly on to the eclipse spectrum.

Earth-like exoplanets

With current capabilities, notably the space-based transit monitors, the detection of Earth-like planets has become feasible. Characterising their atmospheres, however, requires new generations of telescopes and instruments (Perryman et al., 2005; Vázquez, Pallé & Montañés Rodríguez, 2010) and is extremely technically challenging. Also, as we know from studies of the evolutionary history of the Earth's own atmosphere, the inference of the presence of life from the detection of individual molecular species is not without ambiguity. The efforts taking place now to assemble high quality observations of long-pathlength telluric spectra over a wide wavelength range will prove to be of great value in future experiment design. In the visible spectrum, it is fascinating to perceive the direct connection between the telluric spectra and some of the atmospheric phenomena we can see from the surface of our planet.

The colours of the sky are beautiful, rich and varied and the interplay between complex geometry and a small number of scattering and absorption processes can produce the great variety of effects. In addition to developing a close understanding of the formation of the colours we can see, certain geometries allow us to observe rather close analogues of what we might expect to see if we could catch a transiting exo-Earth with a sufficiently large telescope at some — hopefully not too distant — future time. In the visible spectrum, ozone is likely to be one of the most sought after indicators of the state of the atmosphere.

Acknowledgements

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Links

[1] Appleton Water Tower: http://bookings.landmarktrust.org.uk/BuildingDetails/Overview/129/Appleton_Water_Tower
[2] Spectroscopy & Molecular Properties of Ozone project: http://smpo.iao.ru/1188x1216/en/home/

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Four antennas of the Atacama Large Millimeter/submillimeter Array (ALMA) on the Chajnantor plateau profiled against the night sky. The Moon illuminates the scene on the right, while the Plane of the Milky Way stretches across the upper left.