

# First detection of the O III 495.8911 and 500.6843 nm lines in the Earth's upper atmosphere

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**Abstract.** We report the first detection of two emission lines of the atomic oxygen doubly-charged ion at 495.8911 and 500.6843 nm in the terrestrial upper atmosphere. They correspond to the transitions  $^1D_2-^3P_1$  and  $^1D_2-^3P_2$  of the  $O^{++}$  ion, respectively. The measurements were performed on 30 October 2003 during the “Halloween” storms, with the Ultraviolet and Visual Echelle Spectrograph (UVES) mounted on the Very Large Telescope (VLT) in Chile. The intensities of these emissions are  $\sim 70$  mRayleigh, and  $\sim 260$  mRayleigh, respectively. These emissions constitute a new diagnostic of the state of the ionosphere.

**Keywords.** Ionosphere (Ionospheric disturbances)

## 1 Introduction

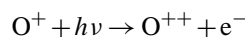
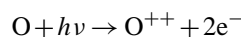
Doubly-charged ions have been studied in laboratories and in the atmospheres of Venus (Fox and Victor, 1981; Gronoff et al., 2007), Earth (e.g. Simon et al., 2005, and references herein), Mars (Witasse et al., 2002, 2003), and Titan (Lilinsten et al., 2005). These species are difficult to measure in the atmosphere because of their low density and their charge to mass ratio which is often equal to another singly-charged ion. They are interesting to study for their exotic or unexpected photo-chemistry and their high reactivity (Thissen et al., 2011). This paper focuses on the  $O^{++}$  ion, which was detected in the terrestrial atmosphere in 1967 by mass spectrometry (Hoffman, 1967). A number of observations and studies have been carried out, to further characterize the production, transport and loss of this ion (e.g. Breig et al., 1977, 1982; Avakyan, 1978; Simon et al., 2005).  $O^{++}$  is produced by photo-ionization and electron impact, and lost by

charge transfer reactions with neutral components of the atmosphere and by radiative recombination with thermal electrons. The fluorescence around 500 nm is well known since it has been used as a tracer of electron densities and temperatures in gaseous nebulae since the 1940s (e.g. Menzel and Aller, 1941). O III night-time auroral emissions in the EUV range have been tentatively reported in Paresce et al. (1983). However, the terrestrial emission in the visible range has never been observed. We report here its first positive detection with the UVES mounted on the VLT in Chile.

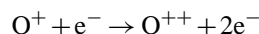
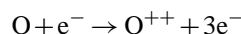
## 2 Photo-chemistry of the $O^{++}$ ion

In the terrestrial atmosphere,  $O^{++}$  is produced by photo-ionization of O and  $O^+$ , and electron impact on O and  $O^+$ . It is lost by reactions with  $N_2$ ,  $O_2$ , and O, and by recombination with free electrons. The list of key processes is given below (see Simon et al., 2005, for more details):

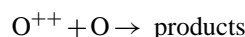
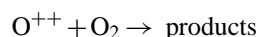
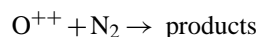
Production (day)



Production (day, aurorae)



Loss (day, night)

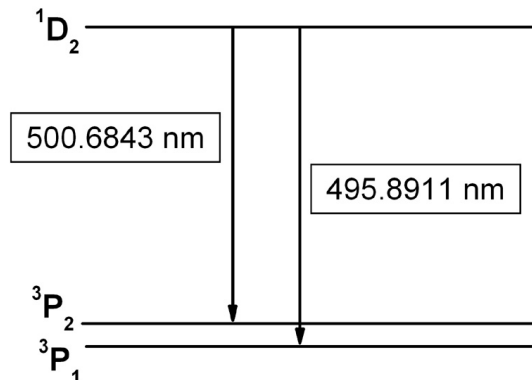
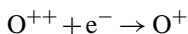


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**Table 1.** O III and N II transitions.

	NIST wavelength (nm)	UVES wavelength (nm)	Energy (eV)	UVES intensity (mR)	UVES width (nm)	Einstein A-coefficient (s <sup>-1</sup> )	Terms	Ji-Jk
O III	495.8911	495.8947	2.51+35.1	70	0.0075	6.21e-03	<sup>3</sup> P- <sup>1</sup> D	1-2
O III	500.6843	500.6845		260	0.0115	1.81e-02	<sup>3</sup> P- <sup>1</sup> D	2-2
N II	654.805	654.8071	1.90+14.534	–	–	9.84e-04	<sup>3</sup> P- <sup>1</sup> D	1-2
N II	658.345	658.3438		400	0.012	2.91e-03	<sup>3</sup> P- <sup>1</sup> D	2-2

Source: National Institute of Standards and Technology (NIST) database (<http://physics.nist.gov>)

**Fig. 1.** Energy levels for O III transitions.

Measurements with mass-spectrometry techniques and modelling agree relatively well on the densities. Typically, the O<sup>++</sup> densities reach 1 cm<sup>-3</sup> at 180 km and 100 cm<sup>-3</sup> at 600 km. The densities are strongly dependent on solar activity latitude and solar illumination, i.e. day or night conditions (Simon et al., 2005).

### 3 Fluorescence

The energies of the first levels for the O<sup>++</sup> doubly-charged ion are given in Fig. 1. Two transitions can occur between the ground-state and the first excited states (between the <sup>3</sup>P ground states, and the <sup>1</sup>D excited state) at the corresponding wavelengths of 495.8911 and 500.6843 nm (see Table 1 and Fig. 1).

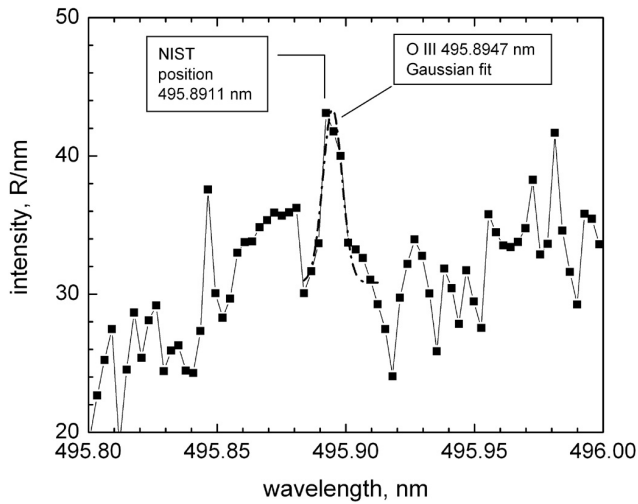
The ratio of intensities of both emissions is given by the ratio of the Einstein coefficients, equal to 2.9 according to the NIST database, a value very close to that of Storey and Zeippen (2000). As mentioned above, no positive detection of these two emissions in the visible range in any planetary atmosphere has been reported so far.

### 4 Observations

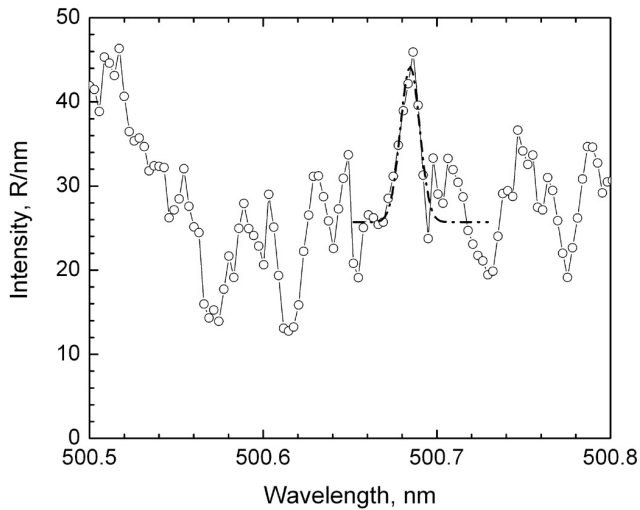
Spectra were obtained with the UVES mounted on the VLT, from 29 October to 2 November 2003. Measurements of O<sup>+</sup> ion and other emissions during the “Halloween” geomagnetic storm were published by Sharpee et al. (2008). All necessary information about these observations can be found in this article and will not be repeated here. A further look at these data indicated the presence of unidentified lines, which we have attributed to the transitions between the <sup>1</sup>D and <sup>3</sup>P levels of the O<sup>++</sup> ion. Figures 2 and 3 display the two spectral regions of interest, around 495.9 and 500.7 nm. The date of acquisition is 30 October 2003. The emission line at 495.8911 nm is actually found at 495.8947 nm. It is 0.0075 nm in width and the intensity is 70 mR. The emission line of 500.6843 nm is found at 500.6845 nm, is 0.0115 nm wide, with an intensity of 260 mR. Both the wavelength and the ratio of intensities are a clear indication that these lines come from the de-excitation of the O<sup>++</sup> ion from the <sup>1</sup>D to the <sup>3</sup>P levels, the analogues of the two optically-forbidden neutral O-atom lines at 630.0 and 636.4 nm.

Many of the features appearing in these spectra are identifiable lines. An atlas has been published (Cosby et al., 2006) in which 2800 lines have been categorized, most of them arising from either O<sub>2</sub> or OH. It is estimated that another 4000 lines can be identified, where the spectroscopic data are now sufficiently precise to calculate positions accurately.

Another isoelectronic system is the <sup>1</sup>D-<sup>3</sup>P multiplet from singly-ionized N. As seen in Fig. 4, these lines appear in the same UVES spectrum. All three of these systems – O III, N II, and O I are calculated to have an intensity ratio – I(<sup>1</sup>D<sub>2</sub> – <sup>3</sup>P<sub>2</sub>)/I(<sup>1</sup>D<sub>2</sub> – <sup>3</sup>P<sub>1</sub>) of 3.0 (National Institute of Standards and Technology (NIST) database). It has previously been shown that this calculation is quite accurate for O I (Sharpee and Slanger, 2006), and evaluation of the UVES data shows that the same holds for N II and O III within substantially larger error limits. The radiative lifetimes of the <sup>1</sup>D levels, as given by the National Institute of Standards and Technology (NIST) database, are 41 s for O<sup>++</sup>, 257 s for N<sup>+</sup>, and 134 s for O. However, the most recent calculations give a value for O(<sup>1</sup>D) of 116 s (Sharpee and Slanger, 2006). Because collisional quenching of these species is expected to be rapid, emission will be seen only from high altitudes.



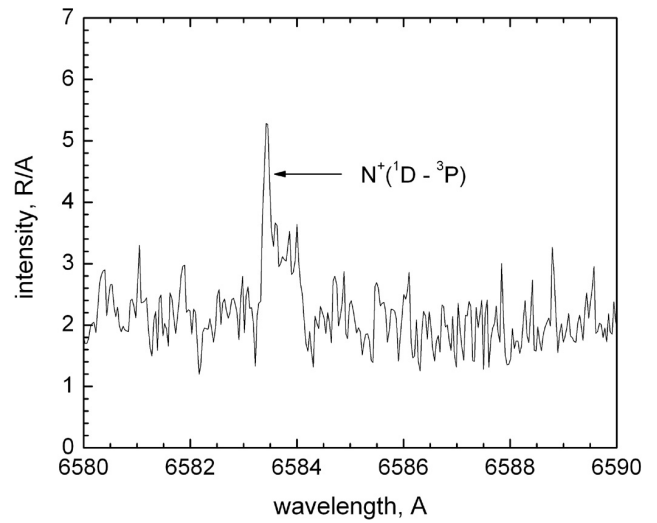
**Fig. 2.** UVES spectrum of the O III  $^1D_2-^3P_1$  line acquired one hour after sunset on 30 October 2003.



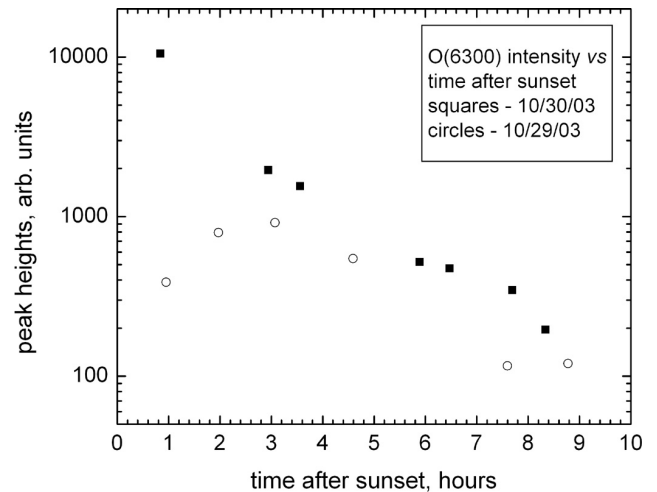
**Fig. 3.** UVES spectrum of the O III  $^1D_2-^3P_2$  line acquired one hour after sunset on 30 October 2003. Fitted wavelength – 500.6845 nm.

For the case of  $O^+(^2D-^4S)$  at wavelengths of 372.603 and 372.882 nm, it was estimated that emission originated above 600 km (Sharpee et al., 2008), although here the NIST lifetime value is much greater than the above values, 5600 s.

High levels of  $O(^1D-^3P)$  red line emission are associated with the geomagnetic storm effects where these ionic species are seen. Figure 5 shows the 630 nm intensity throughout the nights of 29–30 October 2003. One sees that after about three hours after sunset, the intensity is comparable for the two nights, but for the first measurement on 30 October, when the various emissions we have described are at their maximum, the red line intensity is 8 times greater than on 29 October. The scatter in the data is not related to measurement uncertainty, but reflects the fact that the atmosphere is dynamic,



**Fig. 4.** UVES spectrum acquired one hour after sunset on 30 October 2003, showing the NII ( $^1D-^3P$ ) emission line. The fitted wavelength position is 658.3438 nm, with an intensity of 0.4 R, and a width of 0.012 nm. The NIST position is 658.345 nm. Features to the long wavelength side may be nebular emission of the same transition.



**Fig. 5.** Atomic oxygen (630 nm) intensities measured by the UVES/VLT through the nights of 29 October 2003 (open circles) and 30 October 2003 (filled squares). Integration times are 40 min.

long integration times are used, and the viewing directions change throughout the night.

### 5 Discussion

Observations of  $O^{++}$  ions in the terrestrial upper atmosphere with mass spectrometry techniques have shown that the ion density strongly increases during the recovery phase of a geomagnetic storm (Avakyan, 1983; Murphy et al., 1984;

Truhlík, 1997). In Truhlík (1997), an enhancement by a factor of almost 10 has been observed at mid-latitudes, at altitudes above 700 km. During the recovery phase of a geomagnetic storm, outflowing protons transfer momentum to  $O^{++}$  ions by means of collisions. As a consequence,  $O^{++}$  ions are transferred to the outer ionosphere. The UVES/VLT observations reported in this paper were performed during a storm, and this could explain the detection of the O III emissions. However, there is most likely a much better explanation. Mannucci et al. (2005) reported a 900 % increases in total electron content during the “Halloween” storm. The penetration of interplanetary electric fields resulted in the dayside equatorial ionosphere being uplifted (Tsurutani et al., 2006). Ionospheric species are produced on the dayside in the photochemical dominated region and subsequently moved to upper altitudes, where the lifetime of species is much longer against loss via chemistry. This mechanism would explain the UVES observations performed after sunset. However, no definitive explanation as to which mechanisms generate  $O^{++}$  is provided in this article, since it is very difficult to fully assess the state of the upper atmosphere with one observation from a ground-based telescope. Nevertheless, the measurement of these emissions provides a new diagnostic tool for the characterisation of magnetic storms in the terrestrial atmosphere.

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