# The Ionospheric Oxygen Green Airglow: Electron Temperature Dependence and Aeronomical Implications.

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**Abstract.** The laboratory measurement of processes involved in terrestrial airglows is essential in developing diagnostic tools of the dynamics and photochemistry of the upper atmosphere. Dissociative electron recombination of $O_2^+$ in the ionospheric F-region is expected to produce both $O(^1D)$ and $O(^1S)$ which are the sources of the 630.0 nm red airglow and the 557.7 nm green airglow lines, respectively. We present both theoretical and experimental evidence, the latter from a heavy ion storage ring technique, that the $O(^1S)$ quantum yield from $O_2^+(v = 0)$ is a strong function of the electron temperature due to a molecular resonance phenomenon. At present the $O_2^+(v = 0)$ theoretical and laboratory recombination data cannot explain rocket observations of the ionospheric green and red airglows [*Takahashi et al.* 1990; *Sobral et al.* 1992].

## Introduction

The green airglow at 557.7 nm in the terrestrial atmosphere originates from the forbidden $^1S$–$^1D$ transition of atomic oxygen. At lower altitudes (around 90 km), $O(^1S)$ formation is ascribed to oxygen-atom recombination by a two-step 'Barth' mechanism, whereas in the upper atmosphere, dissociative recombination (DR) of $O_2^+$ is believed to be the dominant source of $O(^1S)$ [*Bates* 1990] according to the reaction

$$O_2^+(v) + e^- \rightarrow O + O(^1S) , \qquad (1)$$
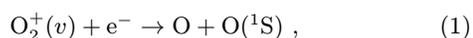
where $v$ labels the vibrational level in the $O_2^+$ electronic ground state. Three factors conspire to make it very difficult to reconcile laboratory measurements of reaction (1) with ground-based and satellite/rocket observations of the green airglow. First, DR may strongly depend on the vibrational state of the parent molecule. It is very difficult to control the vibrational population of the $O_2^+$ ions in a laboratory-plasma [*Zipf* 1988; *Zipf* 1980]. Second, the interpretation of optical measurements in the atmosphere requires a number of collisional quenching rates for the excited oxygen atoms in the background atmosphere, many

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of which have not been measured. Finally, measurements of the quantum yield of $O(^1S)$ from the DR of $O_2^+$ are simply very difficult to achieve in the laboratory. Recently two important steps have been taken towards a better understanding of the green airglow in the F-region. An ion storage ring experiment [*Kella et al.* 1997] provided direct evidence that DR of $O_2^+$ in the lowest vibrational levels leads to a higher yield of $O(^1S)$ than had been anticipated by theory [*Guberman* 1987; *Guberman and Giusti-Suzor* 1991]. In addition, the proposed mechanism for $O(^1S)$ production was revised to include spin-orbit coupling [*Guberman* 1997] which means that $O(^1S)$ quantum yields are now in closer agreement with the above-mentioned data [*Kella et al.* 1997].

## Results

Using the heavy ion storage ring CRYRING at the Manne Siegbahn Laboratory we recently made the first determination, over a fine grid of electron energies, of cross sections and branching over different combinations of oxygen atom pairs yielded by reaction (1). Branching fractions over atom pairs can be recast in quantum yields of the atomic products $O(^1S)$, $O(^1D)$ and $O(^3P)$. From these observations, rate coefficients and quantum yields can be inferred for any electron temperature. We use a high-pressure ($> 0.1$ Torr) hollow cathode ion source in which vibrationally excited $O_2^+$ is largely quenched. Thus we measure reaction (1) for $v = 0$ ions. The $O_2^+$ ions are injected in the ion storage ring and accelerated to 3.06 MeV. The circulating ions interact at each revolution with an intense coaxial electron beam, the energy of which may be accurately tuned. This "merged beam" technique yields a resolution in electron collision energy of about 1.3 meV [*Danared et al.* 1998]. The neutral fragments formed in DR leave the storage ring at the first bending magnet, and enter a 5.9 meter long straight section at the end of which a detector is positioned. The positions and arrival-time difference of the two fragments are measured for each observed event. The distance between the fragments is directly related to their kinetic energy and internal energy. Details of apparatus and method have been published elsewhere [*Rosén et al.* 1998].

In Figure 1, distance spectra are shown indicating that the different atom-pairs are indeed resolved. Results are shown at three electron collision energies. The solid lines are fitted synthetic spectra in which the only free parameters are the branching ratios of the different channels. No effect of $O_2^+(v = 1)$ ions is evident on the position of the $O(^1S) + O(^1D)$ peak. From this we conclude that our beam contains predominantly $O_2^+(v = 0)$ ions. Figure 1a shows that the $O(^1D) + O(^1D)$ pairs can not be fully separated
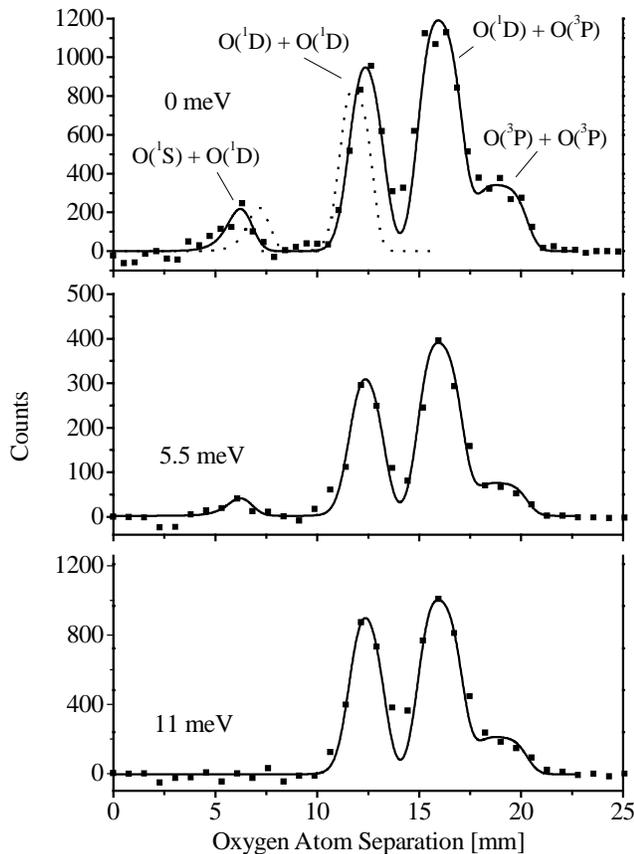
**Figure 1.** Experimental distance spectra. The dissociation limit related to each peak is indicated. Solid lines are synthetic spectra, determined by the energetics of $O_2^+$ and apparatus parameters. The rotational temperature of the ions is assumed to be 300 K, only $O_2^+(v = 0)$ ions are present. A distance spectrum taken with electrons turned off has already been subtracted (occasional small negative counts are a consequence of this subtraction procedure). Three examples of distance spectra are given. Upper panel: 0 meV collision energy. The peak in the dotted line at small separations indicates the position of the $O(^1S)+O(^1D)$ peak expected in the case of $O_2^+(v = 1)$ ions. The second dotted line peak corresponds to $O_2^+(v = 0)$ produced in the $O(^3P)+O(^1S)$ dissociation limit. Center panel: Distance spectra at 5.5 meV. Lower panel: Distance spectra at 11 meV. Note the disappearance of the first peak. Note also that the different total counts for the energies shown simply reflect differences in integration times.

from the $O(^3P) + O(^1S)$ channel, which is the second dissociation limit yielding $O(^1S)$ atoms. We choose to ignore the $O(^3P) + O(^1S)$ channel. This is partly because studies of the electric field-induced dissociation of high Rydberg states of $O_2$ [*Helm et al.* 1996] did not yield any evidence of $O(^3P) + O(^1S)$ atom pair production. Theoretical calculations on the electronic structure of $O_2$ also provide very strong support for the absence of this atom pair [*Guberman* 1983; *Guberman* 1987]. Additional evidence stems from the width of the suprathermal emission line of the green airglow based on a satellite measurement [*Killeen and Hays* 1983]. (However, we note an earlier ground-based measurement [*Hernandez* 1971] which reported positive detection of the $O(^3P) + O(^1S)$ channel). In this work we set the $O(^1S)$ quantum yield equal to the $O(^1S) + O(^1D)$ branching fraction.

Quantum yields measured between 0 and 120 meV are shown in Figure 2a. We observe variation in the $O(^1S)$ quantum yield whereas the $O(^1D)$ quantum yield is found to be $f_D \approx 1.15$, i.e. largely independent of electron energy. This means that the ratio $f_S/f_D$ (and hence the derived relative airglow intensity) is a function of electron temperature only. Experimental uncertainty increases towards higher energies, because it is harder to separate DR signal from background signal owing to a rapid decrease in the total DR rate coefficient. The dot-dashed line is based on an *ab initio* calculation which only takes into account the lower of the $O_2^+(v = 0)$ fine-structure states ($\Omega = 1/2$). The *ab initio* cross section for $O(^1S)$ production has been calculated and convolved to our experimental resolution. We obtain a theoretical quantum yield $f_S$ by dividing the *ab initio* cross section by the total DR cross section measured in our experiment (not shown). Both experiment and calculations predict a drop in quantum yield at the same low energies. Above 100 meV the theoretical quantum yield shows considerable structure which is due to molecular Rydberg resonances.

## Aeronomical Implications

In order to compare our results to atmospheric quantum yields, we thermally average the quantum yields, as shown in figure 2b. The quantum yields have a minimum of 0.016 near 250 K and increase by a factor of 2 for the experimental (cf. 1.7 for the *ab initio*) results between 250 and 800 K. This significant $O(^1S)$ yield for the $O_2^+(v = 0)$ state and the strong dependence on electron energy both have important ramifications. Rocket-borne instruments have inferred $O(^1S)$ quantum yields ranging from 0.09 to 0.23 for measurements between altitudes of 260 to 325 km [*Abreu et al.* 1983] and from 0.02 (at 200 km) to 0.06 (at 320 km) [*Takahashi et al.* 1990; *Sobral et al.* 1992]. Bates has analyzed the latter data [*Bates* 1992] but could not reconcile these observations either with laboratory or with theoretical data.

Figure 3 illustrates the $O(^1S)$ quantum yields as a function of altitude for one set of observations [*Takahashi et al.* 1990] cast into thermally-averaged values of $f_S/f_D$ by Bates [*Bates* 1992] and using our experimental value of $f_D = 1.15$. Also shown are the values of $f_S$ assuming that DR of $O_2^+(v = 0)$ is responsible for the ionospheric $O(^1S)$ yield. The small changes with altitude reflect correspondingly small changes in electron temperature. We note that the electron temperature profile generally follows that of the neutral atmosphere at lower latitudes, although at non-equatorial latitudes the electron temperatures may be as much as 2-3 times larger. The temperature profile used in figure 3 is computed using the MSISE thermosphere model [*Hedin* 1991] for the date of the observations.

Perhaps surprisingly, the quantum yields in figure 3 agree in magnitude, although the rocket data show a much stronger increase with altitude. An unusually large gradient in electron temperature during the actual rocket sounding might be the cause although there are no reasons to expect such a gradient at equatorial latitudes. The use of uncertain quenching rate constants for the metastable fragments in the conversion of observed volume emission rates into quantum yields is certainly a possible explanation, as is the likelihood that other sources of $O(^1S)$ atoms exist. Neither of these possibilities can be ruled out at this stage. However, the contribution of vibrationally excited $O_2^+$ states [*Fox*
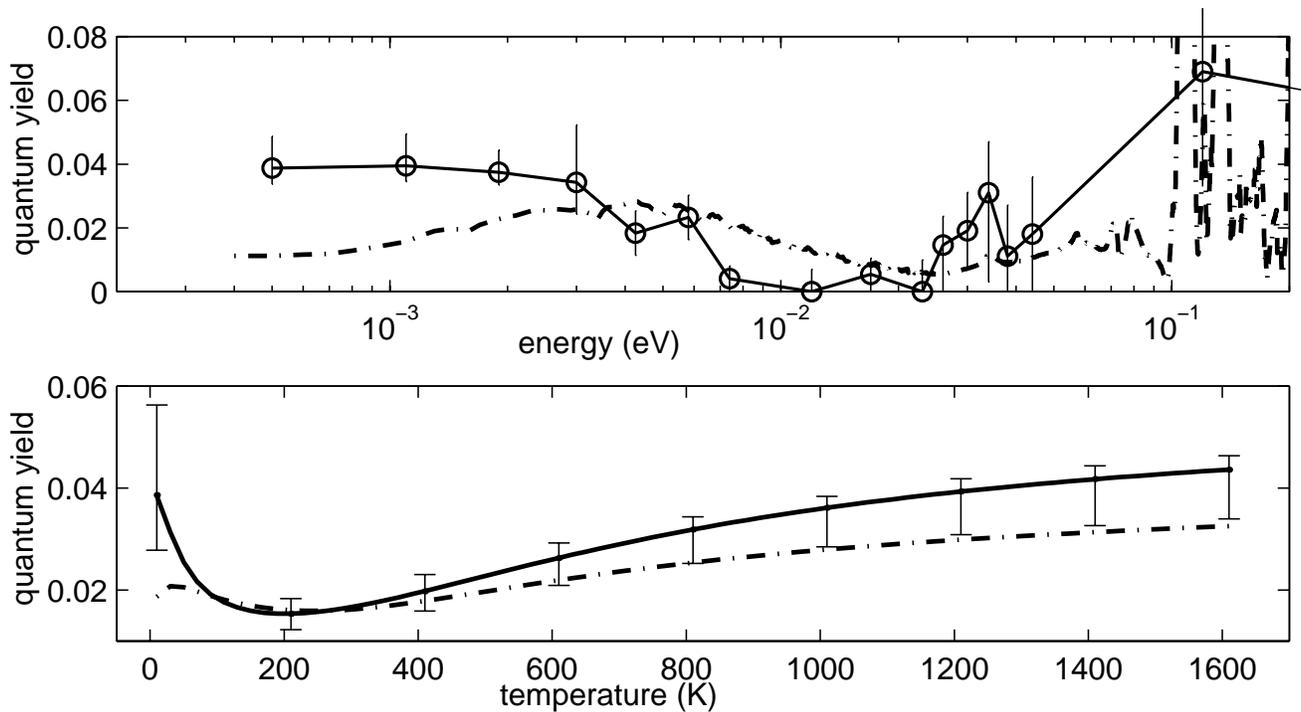
**Figure 2.** Quantum yields as a function of electron energy and temperature. Experimental yields are denoted by solid lines whereas yields from *ab initio* calculations are denoted by dot-dashed lines. Upper panel: Yields as a function of electron energy ($f_S$). The *ab initio* yields have been convolved to the experimental 1.3 meV resolution and divided by the experimental total DR rate (dot-dashed line). Lower panel: Thermally-averaged yields $f_S^{thermal}$.
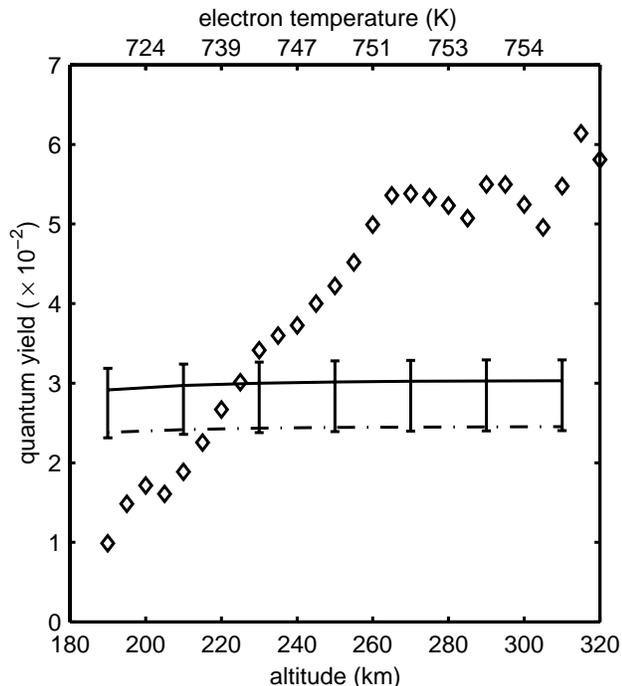


**Figure 3.** Comparison of modelled yields with rocket data. The diamonds show yields $f_s$ inferred from a single rocket measurement [*Takahashi et al.* 1990; *Sobral et al.* 1992]. An analysis by Bates [*Bates* 1992] provided the values for the ratio $f_s/f_D$, for which we assumed $f_D = 1.15$. Thermally-averaged yields derived from the *ab initio* calculation (dot-dashed line) and experimental data (solid line), using an electron temperature altitude profile computed with the MSIS-E thermospheric model, show a very different electron temperature dependence.

1986], which may have larger $O(^1S)$ quantum yields from DR, would be consistent with the largest discrepancies at the highest altitudes and will be tested in a future study.

In summary, we have described the present status of laboratory experiments and theoretical calculations which provide a strong new basis for the analysis of the ionospheric oxygen green airglow. We conclude that the DR process for $O_2^+(v = 0)$ cannot explain rocket observations of the ionospheric airglow [*Takahashi et al.* 1990]. Thus the reasons for the discrepancy between yields inferred from rocket measurements and our modelled laboratory data are still not clear. The discrepancy may arise from other ionospheric sources (i.e. other airglows or vibrationally excited species) or from instrumental sources (i.e. conversion of volume emission rates to quantum yields). Nevertheless, our results reveal that the $O(^1S)$ quantum yield shows a strong dependence on the electron energy (i.e. temperature) where the $O(^1D)$ quantum yield is constant. In principle, the measurement of the relative intensities of the green and red airglow is sufficient to determine electron temperatures in a situation where DR of $O_2^+(v=0)$ ions dominates. Such a measurement does not require knowledge of actual electron and $O_2^+$ densities and may provide a probe of electron temperatures in certain cases.

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