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THE QUENCHING RATE OF O(^{1}D) BY O(^{3}P)

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Abstract—The rate coefficient for the quenching of O(^{1}D) by O(^{3}P) has recently been calculated by Yee *et al.* (1985). Their results indicate that quenching by atomic oxygen should not be ignored in the analysis of the 6300 Å emission airglow. Data obtained by the Visible Airglow Experiment (VAE) on board the *AE* satellites have been reanalyzed to determine the quenching rate of O(^{1}D) by atomic oxygen. The results of this analysis are presented.

1. INTRODUCTION

In studies of the emission of the 6300 Å red line in the day and night airglow, it has been assumed that O(^{1}D) atoms decay by spontaneous radiation

$$O(^1D_2) \rightarrow O(^3P) + h\nu \quad (1)$$

and are quenched by collisions with N_2 and with O_2. At the altitudes where the emission is detected, the abundance of O_2 is much less than that of N_2 and quenching by O_2 may be neglected.

Hays *et al.* (1978) analyzed measurements of the 6300 Å emission taken aboard the *Atmosphere-Explorer C* satellite and, with a spontaneous transition probability A (^{1}D) of 0.0091 s^{-1} (Garstang, 1951), derived a rate coefficient k_{N_2} of 3.0×10^{-11} cm^3 s^{-1}, a value which is higher than the laboratory measurements (Davidson *et al.*, 1976; Streit *et al.*, 1976; Amimoto *et al.*, 1979) of 2.3×10^{-11} cm^3 s^{-1}. A similar analysis was carried out by Link *et al.* (1981) with the transition probability of 0.0068 s^{-1} measured by Kernahan and Pang (1975). Link *et al.* inferred that $k_{N_2} = 2.3 \times 10^{-11}$ cm^3 s^{-1}, apparently resolving the discrepancy with laboratory data. However, an elaborate quantal calculation of the transition probability has been reported by Froese-Fischer and Saha (1983), who obtained the value 0.00934 s^{-1}, close to the original estimate of Garstang (1951), so that the discrepancy persists. Discrepancies were found also by Cogger *et al.* (1980). Quenching of O(^{1}D) in collisions with oxygen atoms has been ignored in the analyses of the emission line data and we suggest that the discrepancy can be removed by postulating an oxygen quenching rate coefficient k_0 of the order of 10^{-11} cm^3 s^{-1}. A rate coefficient of this magnitude is consistent with quantal calculations of the scattering of O(^{1}D) atoms by ground state O(^{3}P) atoms at low energies (Yee *et al.*, 1986).

2. MODEL OF THE 6300 Å EMISSION

In the steady state, the O(^{1}D) atoms, produced by dissociative recombination of O_2^+,

$$O_2^+ + e \rightarrow O + O \quad (2)$$

lead to a volume emission rate at night of 6300 Å photons given by

$$\eta(6300\,Å) = \frac{A(6300\,Å)\beta_{^1D}k_d n(O_2^+)n_e}{A(^1D) + k_0 n(O) + k_{N_2}n(N_2)}, \quad (3)$$

where $A(6300\,Å) = 0.00706$ s^{-1} (Froese-Fischer and Saha, 1983) is the spontaneous transition probability for the $^1D_2$–$^3P_2$ transition, $\beta_{^1D}$ is the quantum yield of O(^{1}D) atoms in the dissociative recombination of O_2^+, k_d is the rate coefficient for dissociative recombination O_2^+, $n(O)$ and $n(N_2)$ are the ambient densities of O and N_2 respectively and N_e and $n(O_2^+)$ are the ambient densities of electrons and O_2^+ molecular ions respectively.

In comparing equation (3) with observations, we adopted for k_d the laboratory values of Walls and Dunn (1974) and for N_2 the measured value 2.3×10^{-11} cm^3 s^{-1}. We determined $\beta_{^1D}$ and k_0 by a least squares fitting of the data seeking the minimum of the quantity

$$\chi^2 = \frac{1}{N}\sum_i (\eta_i - \eta_i^0)^2/\varepsilon_i, \quad (4)$$

where η_i is the value calculated from equation (3), η_i^0 is the observed volume emission rate, ε_i is the estimated error in that observation, and N is the number of data points. The parameter β'_D is a function of electron temperature and depends on the vibrational distribution of the O_2^+ ions. We have used data in which the neutral temperature remained between 700 and 800 K and we expect that the variations in β'_D were minimal.

3. EXPERIMENTAL RESULTS

The data were obtained by the Visible Airglow Experiment (VAE) (Hays *et al.*, 1973) in 17 circular spinning orbits of the *AE-C* and *AE-E* satellites. The VAE measures brightness; the volume emission rate integrated along the line of sight of the observation. In order to determine the volume emission rate itself, we employed a technique involving the subtraction of measured brightnesses obtained along the same direction in inertial space from consecutive satellite spins. Figure 1 illustrates the technique. Because we look at approximately the same volume in space from two directions, we could use the relative magnitudes of the forward and backward observations to reject noisy data.

All data were taken outside the South Atlantic anomaly at solar zenith angles greater than 120°, within ±40° dip latitude and on magnetically quiet days with $K_p < 2$.

The O_2^+ and total ion densities were obtained simultaneously from the Bennett ion mass spectrometer (BIMS) on board (Brinton *et al.*, 1973). The measurements were normalized using a constant normalization factor (1.25 for satellite *AE-C* and 2.26 for satellite *AE-E*), determined from the average ratio of the total ion density measured by BIMS to the total ion density measured by the retarding potential analyzer (RPA) (Hanson *et al.*, 1973). The oxygen and molecular nitrogen densities were measured by the open source spectrometer (OSS) (Nier *et al.*, 1973), and the neutral temperature T_n was measured by the neutral atmosphere temperature experiment (NATE) (Spencer *et al.*, 1973).

The calculation of χ^2 from equation (4) is displayed in Fig. 2. The residuals do not show an absolute minimum but exhibit a valley extending over a range of values of β'_D and k_0. Our data are consistent with earlier atmospheric and laboratory studies (cf. Hays *et al.*, 1978; Link *et al.*, 1981; Abrêu *et al.*, 1983) in indicating that β'_D lies between 0.9 and 1.3. The corresponding values of k_0 lie between 2×10^{-12} cm^{2}s^{-1} and 1×10^{-11} cm^3 s^{-1}. If we choose β'_D equal to 1.2, the derived value of k_0 for all orbits is $(8.0 \pm 7.0) \times 10^{-12}$ cm^3 s^{-1}.

The individual data points are plotted in Fig. 3. The horizontal coordinate is the right hand side of equation (3), omitting β'_D with $k_0 = 8 \times 12^{-12}$ cm^3 s^{-1}. $k_{N_2} = 2.3 \times 10^{-11}$ cm^3 s^{-1}, and the Froese-Fischer and Saha transition probabilities employed. The vertical coordinate is the measured 6300 Å volume emission rate. The slope of the fitted line is then the deduced value of β'_D for this set of assumptions, here equal to 1.2.

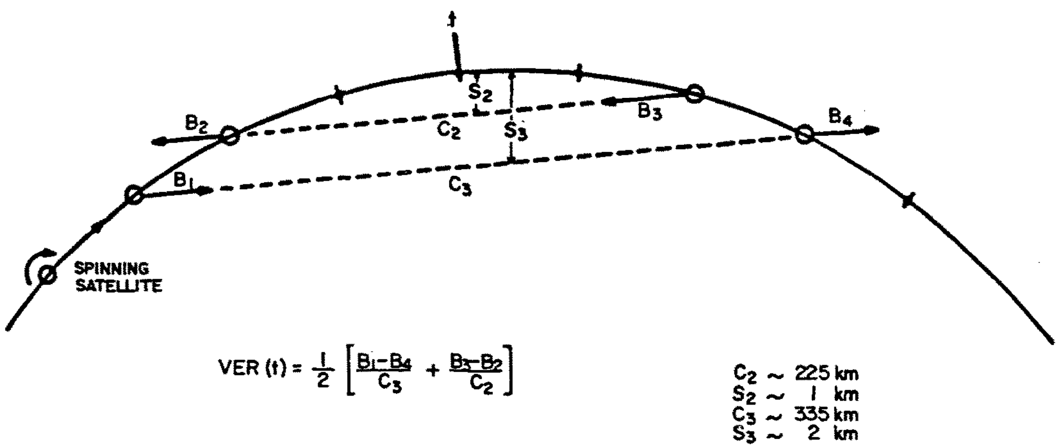

FIG. 1. SURFACE BRIGHTNESS MEASUREMENTS AT THE APPROPRIATE PHOTOMETER ANGLES ARE INTERPOLATED FOR B_1 AND B_4; THE DIFFERENCE IS DIVIDED BY THE LENGTH OF CHORD C_3 TO OBTAIN A VALUE FOR THE EMISSION RATE IN A VOLUME CENTERED AT POINT t.
Then the emission rate is calculated by using B_2, B_3 and C_2. These two values are averaged, and that value is assigned to point t.

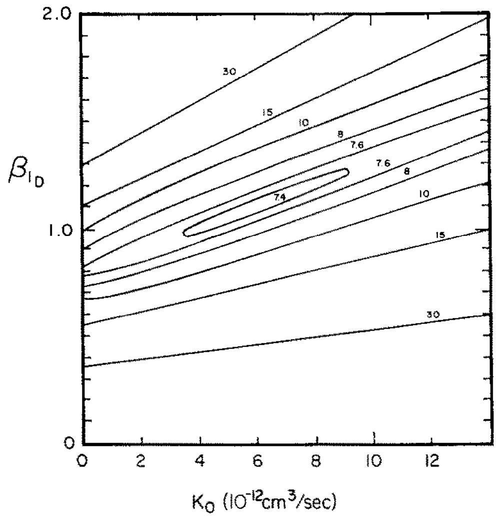

FIG. 2. RESIDUAL CONTOURS CALCULATED FROM EQUATION (4) FOR VARYING VALUES OF $\beta_{^1D}$ AND k_0.
k_{N_2} is fixed at 2.3×10^{-11} cm^3 s^{-1} and the Froese-Fischer and Saha transition probabilities are assumed.

Within the large error bars, the derived oxygen quenching rate coefficient is consistent with the quantal calculations at low collision energies (Yee *et al.*, 1986), and the agreement is sufficient to establish that quenching by oxygen atoms is a significant process in the atmosphere. Because the $O(^1D)$ atoms are produced initially with substantial kinetic energy and are not fully thermalized before radiating, a precise comparison with the quantal calculations must await a determination of the velocity distribution of the ambient metastable atoms.

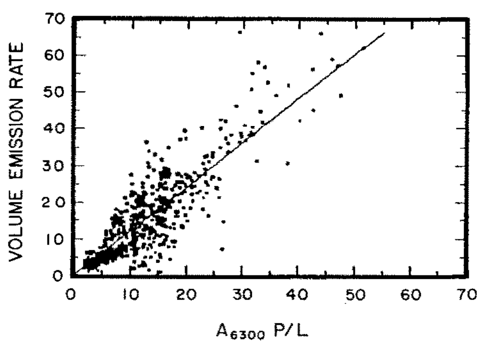

FIG. 3. MEASURED 6300 Å VOLUME EMISSION RATE PLOTTED AGAINST THE RIGHT HAND SIDE OF EQUATION (3) OMITTING $\beta_{^1D}$.
The slope of the fitted line = 1.2 which is the value of $\beta_{^1D}$ for this set of assumed rate coefficients (see text).

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