THERMOSPHERIC PRODUCTION OF O(^{1}S) BY DISSOCIATIVE RECOMBINATION OF VIBRATIONALLY EXCITED O$_2^+$

JENG-HWA YEE and T. L. KILLEEN

Space Physics Research Laboratory, University of Michigan, Ann Arbor, MI 48103, U.S.A.

Abstract—High spectral resolution line profiles at 5577 Å of the night-time, *F*-region O(^{1}S) emission measured by the Fabry–Perot Interferometer on board the *Dynamics Explorer* satellite are analyzed using a continuous O(^{1}S) relaxation model. The model is an improvement over the previous model of Killeen and Hays in that energy loss via elastic collision is considered in addition to the single collision, excitation exchange thermalization process. The results show that the active channel for O(^{1}S) production is capture into the $^1\Sigma_u^+$ repulsive state of O$_2$ and that the main contributor to its production is the dissociative recombination of O$_2^+$ ions in vibrational levels $v = 1$ and 2 in agreement with the quantal calculations of Guberman.

1. INTRODUCTION

The 5577 Å green line emission in the *F*-region of the thermosphere has been studied for many years (Hernandez, 1971; Frederick *et al.*, 1976; Kopp *et al.*, 1977; Bates and Zipf, 1981). The source of the emission at night is believed to be metastable O(^{1}S) atoms produced by the dissociative recombination of O$_2^+$ ions via two possible channels:

$$O_2^+ + e \longrightarrow O_2(^1\Sigma_u^+) \longrightarrow O(^1S) + O(^1D)$$

$$\longrightarrow O_2(^3\Pi_g) \longrightarrow O(^1S) + O(^3P).$$
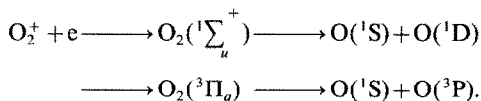
The reactions are exothermic, the excess energy appearing as translational energy of the dissociative fragments relative to the center of mass of the parent molecule. The kinetic energy of formation is gradually lost through collisions with the ambient thermal gases. Because the collisional lifetime at the altitude of O(^{1}S) production is comparable to the radiative lifetime, the non-Gaussian component of the 5577 Å emission line profile is significant (Hays and Walker, 1966; Whipple *et al.*, 1975; Killeen and Hays, 1981).

Analysis of the observed non-thermal line shape can yield information on the initial velocity distribution of the O(^{1}S) atoms and on the collision processes that modify the distribution. Hernandez (1971) demonstrated the non-thermal, *F*-region 5577 Å signature using a ground-based Fabry–Perot interferometer and estimated the branching ratio of the source reaction to be at least five to one in favor of the higher exothermicity channel separating to O(^{1}S)+O(^{3}P). His measurements, however, were

hampered by the brighter, lower O(^{1}S) emission layer near 100 km. Recently, Killeen and Hays (1983) analyzed *F*-region emission line profiles obtained from the Fabry–Perot Interferometer on board the *Dynamics Explorer* Satellite. The profiles were not contaminated by the lower emission layer and they were able to show that, contrary to the conclusions of Hernandez, the lower exothermicity O(^{1}S)+O(^{1}D) channel is favored by at least a factor of four over the O(^{1}S)+O(^{3}P) channel.

There remains an unresolved question concerning the quantum yield of the O(^{1}S) production. Values varying between 2.0% and 9.4% have been determined from various laboratory, ground-based and *in situ* satellite measurements (Bates and Zipf, 1981). It has been suggested by laboratory measurements (Zipf, 1980) and indirect aeronomic studies (Abreu *et al.*, 1983) that the quantum yield is a strong function of the degree of O$_2^+$ vibrational excitation. Abreu *et al.* (1983) concluded that O$_2^+$ vibrational levels other than $v = 0$ give rise to the O(^{1}S) production in the *F*-region, implying that the argument of Bates and Zipf (1981) concerning the rapid quenching of vibrationally excited O$_2^+$ by O may not hold in the night-time thermosphere.

In the present paper, we reanalyze the non-thermal line profiles obtained by the Fabry–Perot Interferometer on *Dynamics Explorer* Satellite reported by Killeen and Hays (1983). The previous model based on thermalization by a single excitation exchange collision is improved by including the slower thermalization process due to elastic collisions. Instead of fitting the observed profiles to obtain an "effective"

thermalization cross section, we use the $O(^1S)-O(^3P)$ collision cross sections for excitation exchange and elastic collisions calculated by Yee and Dalgarno (1985), and analyze the profiles to derive the "most likely" degree of vibrational excitation of the parent molecular ion. The sensitivity of the measured line profiles to the degree of vibrational excitation of the O_2^+ is due to the additional ~ 0.2 eV kinetic energy added to the $O(^1S)$ for each successive increment in v' (vibrational quantum number).

The new results reported here confirm that the $O(^1S)+O(^1D)$ channel is indeed favored in the F-region altitudes and, furthermore, they establish that the O_2^+ ions in vibrational levels $v = 1$ and 2 are the main contributors to the $O(^1S)$ production. These conclusions are consistent with the theoretical calculations of the potential energy curves of O_2^+ given by Guberman (1983), which indicate that only one potential surface $^1\Sigma_u^+$ resulting in $O(^1S)$ is available for an O_2^+ ion in the lowest vibrational levels of the ground state and that it crosses the ion potential surface just above the $v = 1$ vibrational level. The variations in the reported $O(^1S)$ quantum yields are, therefore, most probably the result of different vibrational distributions of O_2^+ ions as suggested by Zipf (1980) and Abreu et al. (1983).

2. $O(^1S)$ NON-THERMAL LINE PROFILES

2.1. Model formulation—continuous relaxation model

The generalized Boltzmann equation which describes the $O(^1S)$ distribution function is usually written

$$\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \frac{\partial \phi}{\partial \mathbf{r}} + \frac{\mathbf{F}}{m} \cdot \frac{\partial \phi}{\partial \mathbf{v}} = \frac{\partial \phi}{\partial t}\bigg)_p + \frac{\partial \phi}{\partial t}\bigg)_r + \frac{\partial \phi}{\partial t}\bigg)_c, \quad (1)$$

where ϕ $(\mathbf{r}, \mathbf{v}, t)$ is the distribution function of the $O(^1S)$ atoms, and the subscripts refer, respectively, to the processes that produce the excited atoms, that remove the excited atoms by radiation and that alter the energies of the excited atoms through collisions. Becauuse the $O(^1S)$ atoms have a short radiative lifetime of 0.90 s, the gravitational force has little effect on the distribution function and we can put $F = 0$. By assuming there is no horizontal and vertical transport of $O(^1S)$ atoms in the regions of interest, we can simplify equation (1) and write it in (z, E, t) phase space as

$$\frac{\partial f}{\partial t} = \frac{\partial f}{\partial t}\bigg)_p + \frac{\partial f}{\partial t}\bigg)_r + \frac{\partial f}{\partial t}\bigg)_c. \quad (2)$$

Equation (2) is very difficult to solve analytically

because of the complicated collision kernel terms on the right-hand side. Here we start with the so-called "one-energy" model and treat the problem numerically. In the one-energy model a number of discrete intervals or energy groups is considered, generating a series of coupled equations for each step in energy. The one-energy Boltzmann equation for $O(^1S)$ atoms with energy E_i can be written as

$$\frac{\partial f_i}{\partial t} = \frac{\partial f_i}{\partial t}\bigg)_p + \frac{\partial f_i}{\partial t}\bigg)_r + \frac{\partial f_i}{\partial t}\bigg)_c. \quad (3)$$

The first term, the energy distribution of a chemical reaction product, was discussed by Whipple et al. (1975) who took into account the initial velocity distribution of the reactants O_2^+ and electrons. For an ambient temperature T, the probability that an $O(^1S)$ atom newly created by dissociative recombination of O_2^+ in vibrational level v has an energy between E_i, $E_i + \Delta E$ is

$$P(E_i) = \int_{\Delta E} \left(\frac{1}{2\pi k T}\right) \exp\left(\frac{E_r}{kT} - \frac{E}{kT}\right) I_0 \, dE, \quad (4)$$

where I_0 is the integral

$$I_0 = \int_{x_0}^{\infty} (x^2 - x_0^2)^{1/2} \{\exp[-(x-v/c)^2]$$
$$- \exp[-(x+v/c)^2]\} \, dx, \quad (5)$$

m_0 and E are the mass and energy of the $O(^1S)$ atom, E_r is the exothermicity of the reaction which depends on v, $x_0 = (2E_r/kT)^{1/2}$, $v = (2E/kT)^{1/2}$, and $c = (2kT/m)^{1/2}$. If we assume isotropic production, $\partial f_i/\partial t)_p$ is given by

$$\frac{\partial f_i}{\partial t}\bigg)_p = [O_2^+][e] \sum_{v=0} k_v g_v P_v(E_i), \quad (6)$$

where k_v is the rate constant leading to the production of an $O(^1S)$ atom for an O_2^+ ion in vibrational level v, g_v is the percentage of O_2^+ ions in vibrational level v and $[O_2^+]$ and $[e]$ are the number densities of O_2^+ ions and electrons respectively.

Because of the short radiative lifetime, the main loss mechanism of the $O(^1S)$ atoms is radiative emission. The radiative loss term is

$$\frac{\partial f_i}{\partial t}\bigg)_r = 1.11 f_i, \quad (7)$$

where 1.11 s^{-1} is the Einstein coefficient for $O(^1S)$ atoms (Nicholaides et al., 1971; Kernahan and Pang, 1975). Collisions with ambient ground state $O(^3P)$ atoms

are the dominant thermalization processes for the newly created O(¹S) atoms. Yee and Dalgarno (1985) have calculated the cross sections for both excitation energy transfer and elastic scattering which occur in an O(¹S)–O(³P) collision. They give a formula for evaluating the rate coefficient for the production of O(¹S) atoms with a specific energy in collisions involving an O(¹S) atom of a given initial energy and the ground state O(³P) atoms of a thermal gas,

$$\alpha_{ij} = \bar{\sigma}_{el} \int_0^\infty \int_{\chi^-}^{\chi^+} \frac{2}{m_0 V} \left(\frac{1}{\pi k T}\right)^{3/2} E_k^{1/2}$$

$$\times \exp\left(-\frac{E_k}{kT}\right) d(\cos\chi) \, dE_k + \bar{\sigma}_{tr} \bar{V}_{ij}$$

$$\times \left(\frac{1}{\pi k T}\right)^{3/2} E_j^{1/2} \exp\left(-\frac{E_j}{kT}\right), \tag{8}$$

where V is the center of mass velocity, χ is the angle between the velocities of the colliding atoms, χ^+, χ^- are maximum and minimum angles of χ consistent with the energy transfer $E_i - E_j$ in an elastic collision, V_{ij} is the angular averaged relative velocity between the two atoms, T is the kinetic temperature of the thermal gas, and $\bar{\delta}_{el}$ and $\bar{\delta}_{tr}$ are the effective elastic scattering and excitation energy transfer collision cross sections of 1.71×10^{-15} cm² and 6.67×10^{-16} cm² respectively. Note that the effective elastic scattering cross section calculated by Yee and Dalgarno (1985) is approximately three times larger than the excitation exchange cross section. This means that any theory of collisional relaxation for O(¹S) must consider both elastic and excitation exchange processes since both can make important contributions to the temporally evolving velocity distribution.

The one-energy continuity equation for O(¹S) atoms in the energy interval E_i, $E_i + \Delta E$ can be written as

$$\frac{\partial N_i}{\partial t} = P(E_i) - 1.11 N_i + \sum_{\substack{j=1 \\ i \neq j}} \alpha_{ji} N_j N_0 - \sum_{\substack{j=1 \\ i \neq j}} \alpha_{ij} N_i N_0, \tag{9}$$

where N_0 is the number density of O(³P) atoms. The step-wise energy distribution of the O(¹S) atoms in the steady-state can then be obtained by solving the series of coupled linear equations,

$$N_i \left\{ \sum_{\substack{j=1 \\ i \neq j}} \alpha_{ij} N_0 + 1.11 \right\} = P(E_i) + \sum_{\substack{j=1 \\ i \neq j}} \alpha_{ji} N_j N_0. \tag{10}$$

2.2. 5577 Å spectral line profile

Observations of the green line emission from a high altitude space platform include the contributions from

different altitudes along the line of sight. In the case of isotropic angular distribution, each individual contribution may be obtained by calculating the component of the O(¹S) velocity along the line of sight and its corresponding Doppler frequency shift,

$$I(z, v_i - v_0) = \frac{\mathring{A}_{5577}}{2} \sum_{j=i}^n \frac{N_j(z, E_j)}{v_j}, \tag{11}$$

where $\mathring{A}_{5577}$ is the spontaneous emission rate for O(¹S)–O(¹D) transition at 5577 Å, v_0 is the frequency at the line center, and v_j is the maximum Doppler shift for energy E_j,

$$v_j = v_0 \frac{\sqrt{2E_j/m_0}}{c}. \tag{12}$$

Since the magnitude of the shift is proportional to the component of the O(¹S) velocity along the line of sight, the energy distribution of O(¹S) atoms at very small energy grids is required to obtain a reliable prediction of the line shape near the line center. To avoid excess computations in the calculation of α in the collision energy transfer terms, we simply interpolate the calculated results for an energy grid of 0.02 eV to give the O(¹S) energy distribution on a grid corresponding to the spectral resolution of the observations.

The emission line shape at a given observational angle is obtained by integrating over the line of sight,

$$I(v) = \int_0^\infty I(z, v) \, ds. \tag{13}$$

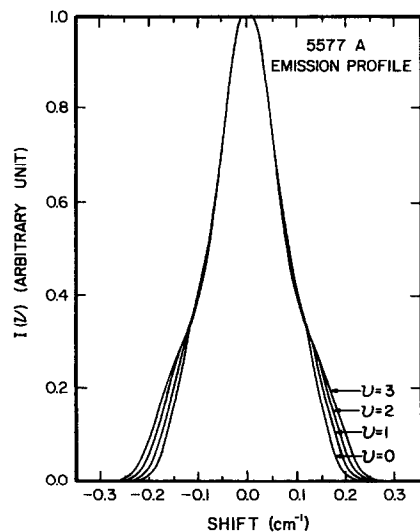FIG. 1. CALCULATED 5577 Å EMISSION PROFILES UNDER THE ATMOSPHERIC CONDITIONS OF ORBIT 6098 FOR THE EXOTHERMIC ENERGIES CORRESPONDING TO $v = 0, 1, 2$ AND 3 RESPECTIVELY.
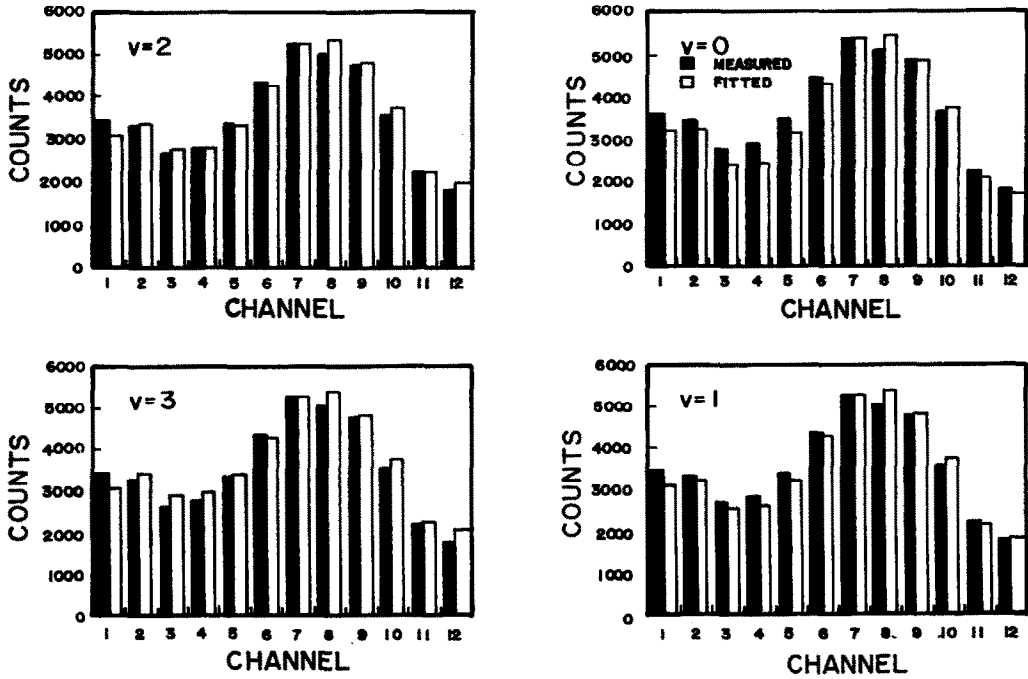
FIG. 2. SIMULATED *DE*-FPI 12 CHANNEL SPECTROGRAMS NORMALIZED TO THE MAXIMUM MEASURED SIGNAL
AT CHANNEL 7 FOR ORBIT 6098.

2.3. *Analysis of* DE-*FPI* 5577 Å *line shape*

The FPI output signal is a convolution of the source function and the instrument transfer function (Killeen and Hays, 1983). The signal may be estimated by using a Fourier representation of the instrument transfer function and performing the convolution in Fourier space using the transform of the source function. The measured profile may then be expressed as

$$
I_c = R(2\pi)^{1/2} \sum_{n=1}^{\infty} \left[A_n \tilde{I}\left(\frac{2\pi n}{\Delta v_{\text{FSR}}} \right) \right.
$$

$$
\times \cos\left(\frac{2\pi n}{\Delta v_{\text{FSR}}} (v_F - v_0) \right) + B_n \tilde{I}\left(\frac{2\pi n}{\Delta v_{\text{FSR}}} \right)
$$

$$
\left. \times \sin\left(\frac{2\pi n}{\Delta v_{\text{FSR}}} (v_F - v_0) \right) \right],
$$
(14)

where $\tilde{I}$ is the Fourier transform of the source function (13), R is the emission line surface brightness, Δv_{FSR} is the free spectral range of the interferometer, v_F is a reference wavenumber, and A_n, B_n are the Fourier series coefficients of the instrument function (Hays *et al.*, 1981; Killeen and Hays, 1983). A full descrip-

tion of the Fabry–Perot (*DE*-FPI) on *Dynamics Explorer–B* Satellite has been given by Hays *et al.* (1981).

The 5577 Å line shape measured by *DE*-FPI reflects the steady-state energy distribution of the emitting $O(^1S)$ atoms. The distribution depends upon the initial energy of the products in a dissociative recombination reaction, characterized by T_i, T_e, and the exothermic energy and on the thermalization rate by collisions with ambient oxygen atoms. The thermalization rate can be calculated by using the formula of Yee and Dalgarno (1985) and the temperature and atomic oxygen number density can be obtained either from direct measurements with instruments on board *DE* (Carignan *et al.*, 1981; Killeen and Hays, 1983) mapped down to the altitudes of interest, or from the MSIS model (Hedin *et al.*, 1977). We assume that at night, $T_i = T_e = T_n$ for the low latitude measurements analyzed here.

Among the channels which lead to $O(^1S)$ production in a dissociative recombination reaction, the $O(^1S)+O(^1D)$ channel has been found to be strongly favored (Guberman, 1983; Killeen and Hays, 1983). The initial $O(^1S)$ energy distribution depends mainly upon the exothermic energy available and varies with the vibrational distribution of the O_2^+ ions. Table 1

TABLE 1. EXOTHERMICITY FOR VARIOUS
VIBRATIONAL LEVELS OF O$_2^+$

Vibrational level	ER (eV)
0	0.83
1	1.0624
2	1.2948
3	1.5272
4	1.7595

lists the exothermic energy shared by the two product atoms for the first five vibrational levels of O$_2^+$ ions. The observed line profile can be fitted to the results obtained from equation (14) to estimate the contribution of each vibrational level. This is achieved by finding a calculated profile with the least deviation from the measured profile,

$$\chi^2 = \sum_{j=1}^{12} [I_{\text{obs}}(j) - I_{\text{cal}}(j)]^2$$

where $I_{\text{obs}}(j)$ and $I_{\text{cal}}(j)$ are the signals at channel j for the observed line profile and fitted line profile respectively.

3. MEASUREMENTS AND ANALYSIS

The line profiles obtained in the same four perigee passes of the DE-B satellite used by Killeen and Hays (1983) have been re-analyzed. The passes were selected from the data base for periods when the perigee of the orbit was located at equatorial latitudes near local midnight where the enhanced emission region of the F-region tropical arcs is located (Van Zandt and Peterson, 1968).

Figure 1 gives the calculated 5577 Å emissions profiles under the atmospheric conditions of orbit 6098 for the exothermic energies corresponding to $v = 0$, 1, 2 and 3 respectively. Each step of the increase in the vibrational energy of O$_2^+$ ions, approximately 0.2 eV for $\Delta v = 1$, enhances the average energy of the O(^{1}S) atoms and broadens the shoulder of the emission line profile. Figure 2 shows the simulated DE-FPI 12 channel spectrograms normalized to the maximum measured signal at channel 7. The observed spectrogram is given for comparison.

There are differences, particularly in the wings of the profile, between the measured and the simulated profiles. The best fit to the measured profile can be obtained by finding the minimum χ^2 value method. Three additional orbits were also analyzed in the similar fashion. Table 2 lists the atmospheric parameters used in the fitting for these four independent orbits
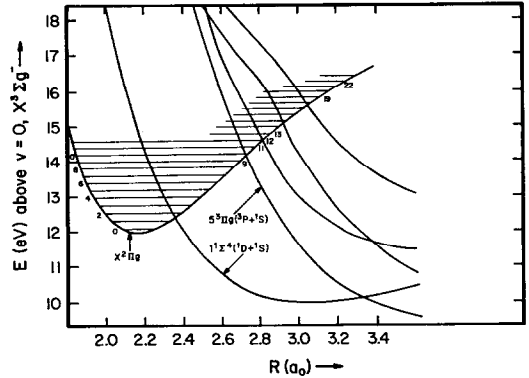

FIG. 3. POTENTIAL ENERGIES CURVES WHICH LEADS TO O(^{1}S) FROM DISSOCIATIVE RECOMBINATION OF O$_2^+$ (GUBERMAN, 1983).
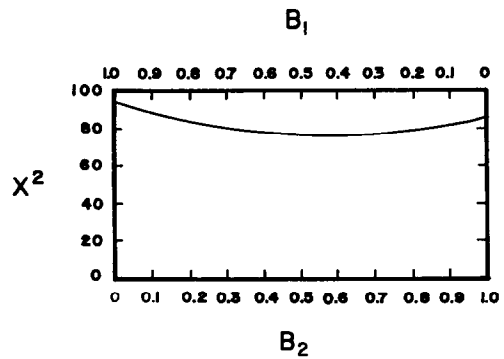

FIG. 4. χ^2 VALUES OF ORBIT 6098 AS A FUNCTION OF RELATIVE CONTRIBUTION β, FROM O$_2^+$ IONS IN THE $v = 1$ OR 2 VIBRATIONAL LEVELS.

and the values of χ^2. The results demonstrate consistently that the minimum χ^2 occurs when the O(^{1}S) atoms are produced with an energy corresponding to a dissociative recombination of O$_2^+$ ions in the $v = 1$ or 2 levels. The results are consistent with the theoretical calculations of the potential surfaces of O$_2^+$ by Guberman (1983) reproduced in Fig. 3, which indicate that only one repulsive $^1\Sigma_u^+$ curve resulting in an O(^{1}S) atom is available for O$_2^+$ ions in the lowest vibrational levels, and that it crosses the ion potential curve just above the $v = 1$ vibrational level of the O$_2^+$ ground state.

In the night-time thermosphere, the O(^{1}S) atoms are produced from the dissociative recombination of O$_2^+$ ions in all its vibrational states. Figure 4 gives the χ^2 values of orbit 6098 as a function of the relative contribution from O$_2^+$ ions in the $v = 1$ or 2 vibrational levels if we assume that all the O(^{1}S) atoms are produced from these two levels. Figure 5 shows the best fit to the measured spectrogram. Because

TABLE 2. FPI χ^2 ANALYSIS

Orbit	Alt (km)	$N(O)$	T_0	R	$v = 0$	$v = 1$	$v = 2$	$v = 3$
							χ^2	
97	220	4.15×10^9*	895*	61	83.8	60.6	*54.7*	57.8
2155	240	4.15×10^9*	850*	88	41.4	*21.6*	57.0	117.7
6098	220	2.00×10^9†	962‡	162	276.6	94.7	*87.4*	146.3
6103	230	1.80×10^9†	913‡	92	226.4	*188.8*	200.1	234.8

* MSIS value.
† NACS value mapped down to altitude of emission.
‡ FPI value from 6300 Å line profile measurement.
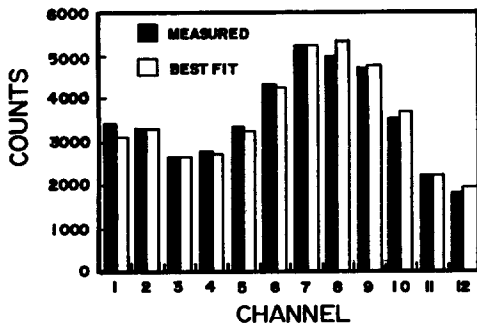The minimum value is in italics.

FIG. 5. THE BEST FIT TO THE MEASURED SPECTROGRAM FOR ORBIT 6098 ($\beta_1 = 0.4$ AND $\beta_2 = 0.6$).

the dissociative recombination rate coefficient for the $v = 0$ level of O_2^+ is much smaller than the rates for $v = 1$ and 2 (Guberman, private communication), we believe that capture from the $v = 0$ level is negligible despite the large population of O_2^+ ions in the ground vibrational level. The results indicate that approximately 60% of the $O(^1S)$ atoms are produced by the O_2^+ ions in the $v = 2$ level. We cannot determine the vibrational population of O_2^+ ions because the specific dissociative recombination coefficients for different vibrational levels are unknown. The vibrational populations will depend upon the atmospheric conditions and give rise to varying quantum yields (Bates and Zipf, 1981; Abreu et al., 1983).

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