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Determination of the Quenching Rate of the O(^{1}D) by O(^{3}P) From Rocket-Borne Optical (630 nm) and Electron Density Data

J. H. A. SOBRAL, H. TAKAHASHI, M. A. ABDU, P. MURALIKRISHNA, Y. SAHAI, C. J. ZAMLUTTI, E. R. DE PAULA, AND P. P. BATISTA

Instituto Nacional de Pesquisas Espaciais, São José dos Campos, São Paulo, Brazil

The quenching rate k_7 of the O(^{1}D) by O(^{3}P) in the nocturnal F region is evaluated on the basis of rocket-borne photometric and electron density measurements that have been carried out aboard a Brazilian Sonda III rocket launched from Natal (geography 5.8°S, 35.2°W) on October 31, 1986, at 2259 Local Standard Time (LST). The nightglow emission and electron density vertical profiles were obtained respectively from a 630-nm photometer and a high-frequency capacitance probe. The quenching rate k_7 was evaluated from model calculations of the OI 630-nm emission rate, utilizing as input data the measured electron density. Assuming the value of 1.1 for the quantum yield factor f(^{1}D) a mean value estimated for k_7 turned out to be 9.2×10^{-13} cm^3 s^{-1}, the upper and lower limits being 2.8×10^{-12} cm^3 s^{-1} and zero, respectively. On the other hand, assuming *Bates'* [1990] height profile of Franck-Condon f(^{1}D) for this same experiment, k_7 resulted in 2.55×10^{-12} cm^3 s^{-1}. These results are discussed and compared with previous measurements from other authors.

INTRODUCTION

The ionosphere-thermosphere system has been utilized with remarkable success in the last four decades as a natural laboratory for a variety of studies concerning atomic and molecular processes in the Earth's upper atmosphere. In particular, among the chemical reactions that have been extensively studied in the past few decades, the dissociative recombination of O_2^+ has received demanding attention since the early investigations by *Bates and Massey* [1947] and *Bates*, [1950]. That reaction plays a fundamental role in the generation of two of the most important emission lines widely used for ionospheric studies, that is, the 557.7-nm and 630-nm emissions. These emission lines have been proven to be very efficient both for the studies of dynamical phenomena and for the chemical processes that take place in the ionosphere-thermosphere system.

A large number of aeronomic studies on the O_2^+ dissociative recombination process utilizing in situ as well as laboratory measurements have appeared in literature, especially during the last two decades. They have rendered important contributions towards the knowledge of the processes of activation and deactivation of excited thermospheric atomic and molecular oxygen [*Dalgarno*, 1958; *Dalgarno and Walker*, 1964; *Peterson et al.*, 1966; *Mehr and Biondi*, 1969; *Hernandez*, 1971; *Brown and Steiger*, 1972; *Hays and Sharp*, 1973; *Frederick et al.*, 1976; *Torr et al.*, 1976; *Kopp et al.*, 1977; *Sobral*, 1978; *Mul and McGowan*, 1979; *O'Neil et al.*, 1979; *Sharp and Torr*, 1979; *Bates and Zipf*, 1980; *Link et al.*, 1981; *Torr and Torr*, 1981, 1982; *Killeen and Hays*, 1983; *Abreu et al.*, 1986; *Rees*, 1984; *McDade and Llewellyn*, 1984; *Guberman*, 1987, 1988; *Link and Cogger*, 1988; *Zipf*, 1979, 1980, 1988; *Yee et al.*, 1985, 1990; *Takahashi et al.*, 1990; *Sobral et al.*, 1992].

Quantitative aspects of the collisional deactivation rates of the atomic and molecular oxygen in the upper atmosphere have been critically reviewed in the last four decades, with particular attention focused on the requirements of sufficient accuracy for aeronomic studies, particularly those concerning the modeling of the OI 630-nm nightglow. The dissociative recombination of O_2^+ is the main source of the atomic oxygen excited species O(^{1}D) and O(^{1}S) in the nocturnal F region. The O(^{1}D), which is the source of the F region 630-nm nightglow, gets partially deactivated by collisions with the atmospheric neutral molecules N_2, O_2, and O and with electrons. The deactivation of O(^{1}D) by collisions with atomic oxygen is given by

$$O(^1D) + O(^3P) \xrightarrow{k_7} O(^3P) + O(^3P), \qquad (1)$$

where k_7 denotes reaction rate. The importance of this reaction, however, became recognized only recently by *Yee et al.* [1985] and *Abreu et al.* [1986] who pointed out that the deactivation process from such reaction may play a substantial role in the emission intensity of the OI 630-nm nightglow.

Abreu et al. [1986] calculated the magnitude of k_7 utilizing in situ measurements of [e], [O] and [N_2] which were not necessarily coincident in space with their airglow measurements. The present study, however, utilized in situ measurements of [e] and OI 630-nm emission rate, and model (mass spectrometer/incoherent scatter (MSIS) 86) [Hedin, 1987] neutral constituents concentrations appropriate for the day of the experiment.

The purpose of this paper is to provide an estimation of the rate coefficient k_7 of reaction (1) based on photometer and plasma probe data obtained from a rocket experiment that was carried out by Instituto Nacional

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de Pesquisas Espaciais (INPE) at Natal on October 31, 1986 at 2259 LST (or November 1, 0159 Universal Time).

CALCULATION OF k_7

Reaction rate k_7 has been estimated here by means of successive adjustments in its magnitude in the expression for the OI 630-nm volume emission rate V_{630} shown below, so that the calculated total nightglow intensity matches the measured total magnitude of the emission rate as observed by the rocket-borne photometer along the zenith direction. V_{630} is given by

$$V_{630} = 0.756 f(^1D) k_3 [O_2][e] / \{([e]/[O^+]) \cdot (1 + (k_2[N_2] + (k_5[O_2] + k_6[e] + k_7[O])/A_{1D}))\} \quad (2a)$$

where A_{1D} is the Einstein transition coefficient for the $O(^1D)$ state ($A_{1D} = A_{630} + A_{636.4} + A_{639.2} = 7.45\times10^{-3}$ s^{-1}, $A_{630} = 5.63\times10^{-3}$ s^{-1}, $A_{636.4} = 1.82\times10^{-3}$ s^{-1}, $A_{639.2} = 8.92\times10^{-7}$ s^{-1} [see *Link and Cogger*, 1989]); V_{630} units is number of photons cm^{-3} s^{-1}; the ratio $[e]/[O^+]$ is assumed to be equal to unity; $f(^1D)$ is the $O(^1D)$ quantum yield in O_2^+ dissociative recombination; and the ki variables are reaction rates as follows:

$$O_2 + O^+ \xrightarrow{k_3} O_2^+ + O \quad (k_3 = 1.06 \times 10^{-11} cm^3 s^{-1}) \quad (2b)$$

$$O(^1D) + N_2 \xrightarrow{k_2} O(^3P) + N_2 \quad (k_2 = 2.30 \times 10^{-11} cm^3 s^{-1}) \quad (2c)$$

$$O(^1D) + O_2 \xrightarrow{k_5} O(^3P) + O_2 \quad (k_5 = 3.20 \times 10^{-11} cm^3 s^{-1}) \quad (2d)$$

$$O(^1D) + e \xrightarrow{k_6} O(^3P) + e \quad (k_6 = 6.60 \times 10^{-10} cm^3 s^{-1}) \quad (2e)$$

$$O(^1D) + O \xrightarrow{k_7} O(^3P) + O \quad (k_7 \text{ to be determined}). \quad (2f)$$

The values of the ki variables listed above were derived from the theoretical expressions shown in *Link and Cogger's* [1988] Table 1, adopting the exospheric temperature of 750°K which is the atmopheric model MSIS 86 [Hedin, 1987] temperature prediction for the date and location of this experiment. The values of $f(^1D)$ used here are the following ones: 1.1, the Franck-Condon and the peaked $f(^1D)$. The first value represents a fair estimate of $f(^1D)$ [*Bates*, 1990, section 2.5]. The latter two values were taken from *Bates* [1990, Table 13].

The measured total intensity I_{630} for the OI 630-nm nightglow, in Rayleigh units R, as seen vertically upward from below the emitting layer, resulted to be 310R ± 30R [*Takahashi et al.*, 1990], the upper and lower limits being 340R and 280R, respectively. These intensity limits were used in this work in the determination of the lower and upper bounds of k_7, respectively. The rate coefficient k_7 has been calculated here utilizing the following expression:

$$V_{Total} = \sum_h V_{630}.\Delta h \quad (3)$$

where V_{Total} (photons cm^{-2} s^{-1}) is the total, or height-integrated, magnitude of the OI 630-nm emission rate.

Assuming $f(^1D)$ was equal to 1.1, the calculated magnitude range for k_7 turned out to be from zero to 2.77×10^{-12} cm^3 s^{-1} corresponding to the measured nightglow error bar of 280R/340R. Notice that adopting k_7=0, which is the lower limit for k_7, I_{630} becomes equal to 328R, which is smaller than the experimental uncertainty upper bound 340R. The measured average magnitude 310R can be theoretically attained if k_7 is assumed to be equal to 9.2×10^{-13} cm^3 s^{-1}.

It should be pointed out that the upper and lower bounds for k_7 discussed above have been estimated as a function of the error bars of the measured I_{630} only. The atmospheric model uncertainty, on the other hand, is of the order of ± 7.5%.

Adopting now *Bates'* [1990, Table 13] Franck-Condon height profile for $f(^1D)$ and expression (3) of this work, the k_7 magnitudes are found to lie in the range of 1.03×10^{-12} (340R) to 4.01×10^{-12} (280R) cm^3 s^{-1} and have average magnitude equal to 2.55×10^{-12} cm^3 s^{-1} (adopting this k_7 value, I_{630} will result to be equal to the observed 310R).

If k_7 is assumed to be equal to the average value of 9.20×10^{-13} cm^3 s^{-1} as cited above and $f(^1D)$ is as Bates' Franck-Condon, then I_{630} (total) = 342.2R.

DISCUSSION

The experiment concerned here consisted of electron density and photometric (OI 630-nm) measurements in the nocturnal F region by means of a photometer and a high- frequency capacitance probe installed aboard a sounding rocket. The experimental electron density data made possible the calculation of the OI 630-nm emission rate height profile that would match the measured OI 630-nm emission rate profile through adjustments in the magnitude of the quenching coefficient k_7. In this way an attempt was made to infer an estimate for k_7.

Two of the height profiles of the OI 630-nm emission rate shown in Figure 1 were calculated assuming $f(^1D)$ to be equal to 1.1 and to match the I_{630} measurement uncertainty limits 310± 30R. For those two profiles the values of k_7 varied from zero to 2.77×10^{-12} cm^3 s^{-1}, the average magnitude being 9.2×10^{-13} cm^3 s^{-1}, as described above.

For the sake of comparison we carried out calculations of V_{630} based on previously published values of k_7 utilizing the same atmospheric model and quenching scheme as described in the last section. The results are shown in Figure 2. The rate coefficients shown in this figure include those reported by *Abreu et al.* [1986] from aeronomic determination ($8(\pm 7)\times10^{-12}$ cm^3 s^{-1}) and by *Yee et al.* [1990] from one of their potential curves (10^{-11} cm^3 s^{-1}; factor of 2 uncertainty).

The total nightglow intensities in Rayleigh units cor-

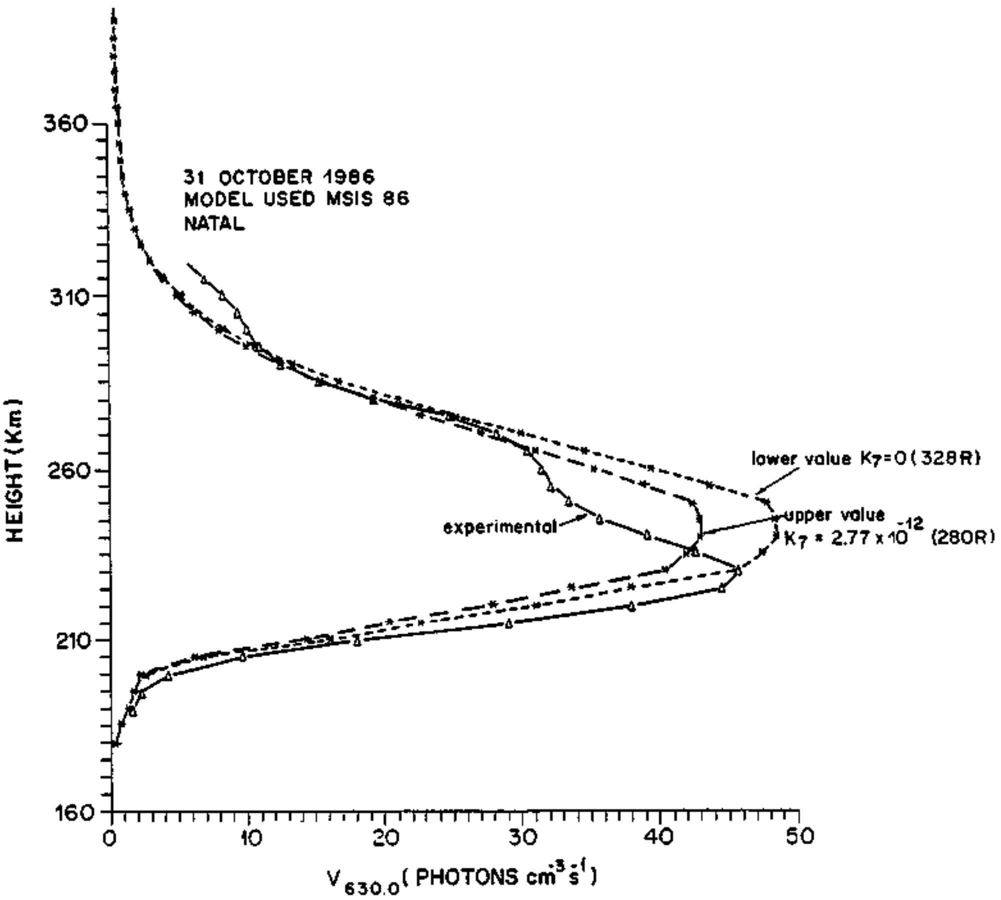

Fig. 1. Experimental and theoretical profiles of the OI 630 nm emission rate V_{630}. The theoretical profiles were made adopting k_7 magnitudes such that the height- integrated calculated nightglow intensity I_{630} would more closely fit the total measured nightglow intensity (310R±30R). k_7 is the rate coefficient of the $O(^1D)$ quenching process via collisions with atomic oxygen.

responding to these profiles are shown near the k_7 values in the same Figure 2.

Yee et al.'s [1990] theoretical prediction of 10^{-11} $cm^3\ s^{-1}$ is found to be too high compared with the present estimate of k_7, since even considering their lowest value of 5×10^{-12} $cm^3\ s^{-1}$ the I_{630} predicted magnitude (250R) comes out to be smaller than the experimental lower bound of 280R.

Considering, however, the other potential curve of Yee et al. [1990], the calculated quenching rate of about $8.1\text{x}10^{-12}$ $cm^3\ s^{-1}$ will result, which, assuming a maximum error of a factor of 2 as cited in that paper, implies a lower bound of 4.05×10^{-12} $cm^3\ s^{-1}$. That value is fairly close to the upper limit found here of 4.01×10^{-12} $cm^3\ s^{-1}$.

It would be interesting to verify what sort of magnitudes would result for k_7 by means of the same type of calculation done above but utilizing other acceptable values of $f(^1D)$.

Bates [1990] shows in his Table 13 two theoretical profiles of $f(^1D)$ versus height that have been calculated for this same experiment. One of them corresponds to the Franck-Condon (FC) vibrational distribution of the O_2^+ ions and the other one corresponds to the peaked (P) distribution. Utilizing the former distribution the range found for k_7 varies from 1.02×10^{-12} to 4.01×10^{-12} $cm^3\ s^{-1}$. Figure 3 shows two profiles of V_{630} that correspond to the average and upper values of the measured integrated nightglow intensities.

Figure 4 is the same as Figure 3 except that it concerns the peaked distribution $f(^1D)$. It is seen that assuming k_7 is equal to zero, I_{630} totals just 259R which is smaller than the observed lower bound 280R. According to this result, one may conclude therefore that the $f(^1D)$, as provided by the peaked distribution, has insufficient magnitude.

Assuming the average magnitude for k_7 previously found, that is, 9.2×10^{-13} $cm^3\ s^{-1}$, and the $f(^1D)$ as given by the peaked distribution,the total nightglow intensity results to be equal to 242R which is about 78% of the value (310R) obtained by considering $f(^1D)$ equal to 1.1.

The emission rate profile of Figure 4 presents a sharp discontinuity at the peak which does not appear too realistic considering the smooth density profiles of the neutrals and electron density.

The range of the k_7 magnitude found in this work is consistent with those of *Abreu et al.* [1986] and *Yee et al.* [1990]. Figure 5 shows a plot of those ranges. The k_7 range that resulted from the Franck-Condon $f(^1D)$ pro-

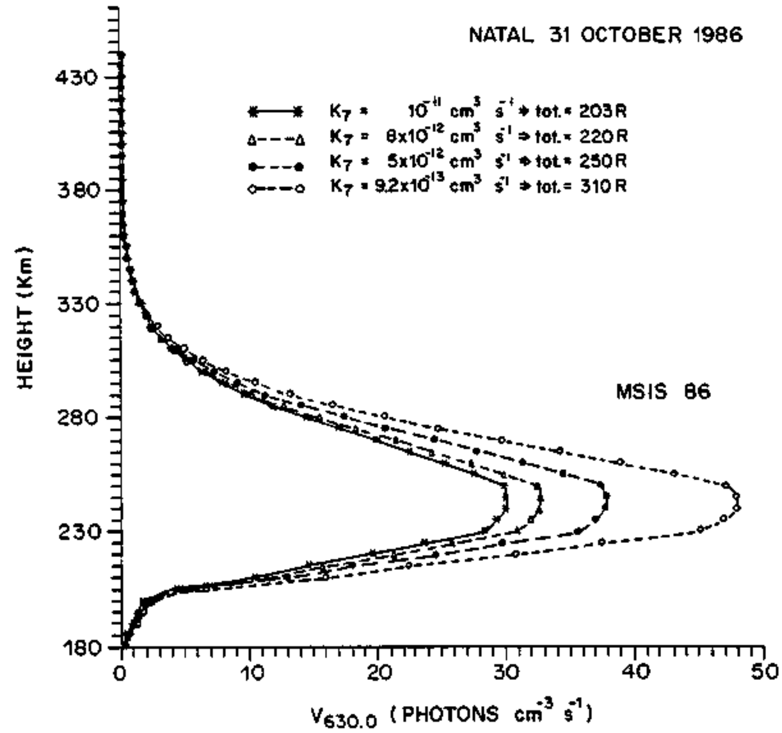

Fig. 2. V630 for various k_7 (cubic centimeters per second) magnitudes: 10^{-11}, 5×10^{-12} [*Yee et al.*, 1990], 8×10^{-12} [*Abreu et al.*, 1986], and 9.2×10^{-13} (this work). The corresponding total nightglow intensity in Rayleigh units is indicated against the rate coefficients.

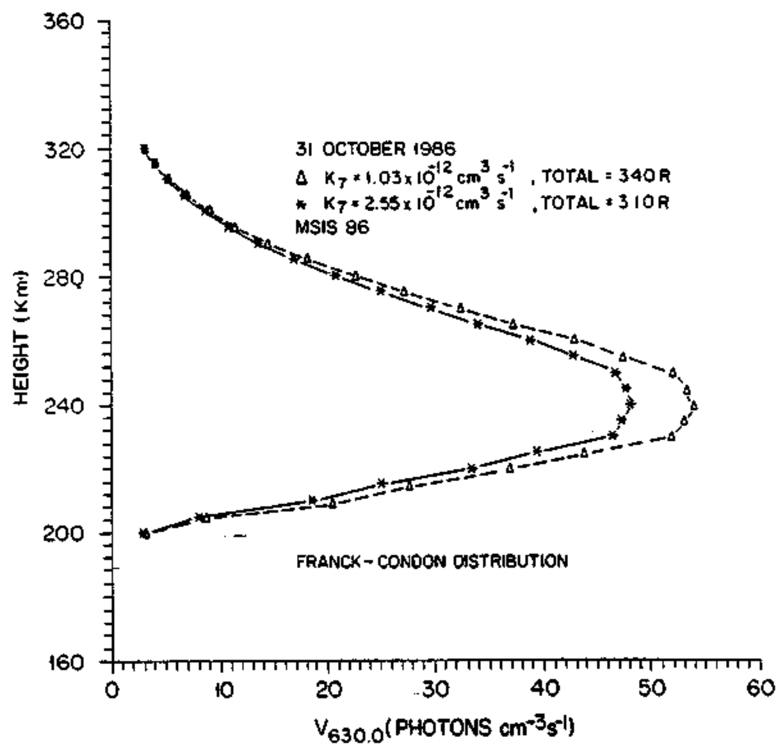

Fig. 3. Theoretical profiles of the V_{630} utilizing *Bates'* [1990] Franck-Condon $f(^1D)$ values (see text). variable 310R corresponds to the experimental mean integrated OI 630-nm nightglow intensity (I_{630}) as measured by the rocket-borne photometer whose line of sight was directed vertically upward from below the emitting layer. 340R refers to the upper end of the error bar in the experimental I_{630}.

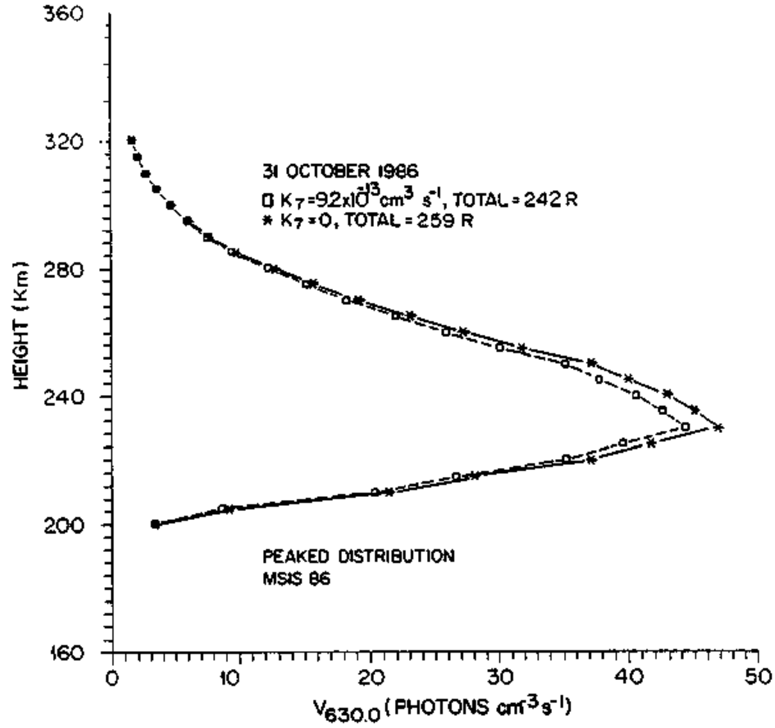

Fig. 4. Same as Figure 3 except that in this case *Bates'* [1990] peaked $f(^1D)$ values are used.

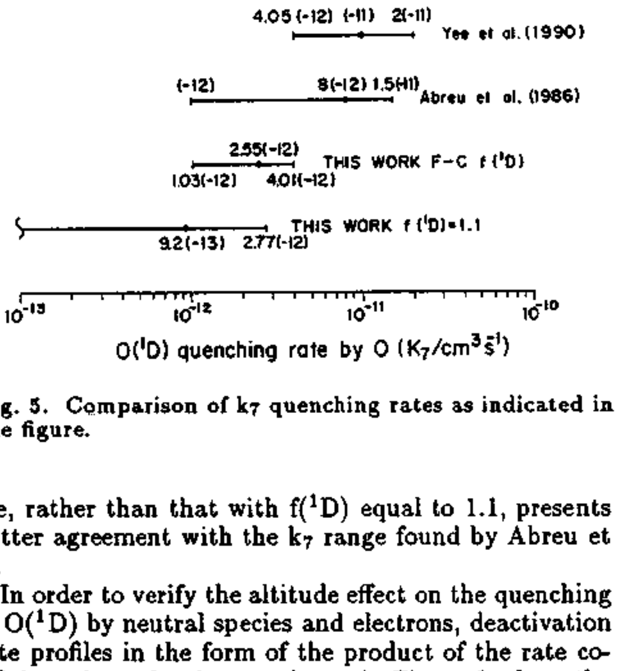

Fig. 5. Comparison of k_7 quenching rates as indicated in the figure.

file, rather than that with $f(^1D)$ equal to 1.1, presents better agreement with the k_7 range found by Abreu et al.

In order to verify the altitude effect on the quenching of $O(^1D)$ by neutral species and electrons, deactivation rate profiles in the form of the product of the rate coefficient times density are shown in Figure 6 where the height interval corresponding to the data points is 5 km. Also shown is the photoemissive deactivation rate 7.45×10^{-3} s^{-1} represented by the dashed line [*Link and Cogger,* 1989] which corresponds to the Einstein coefficient A_{1D}, as previously discussed. To the right of this line is the overall deactivation rate which includes collisional quenching and photoemissive deactivation. The rate coefficients that have been used in the calculations of the profiles of this figure are as in the reactions (2b) to (2e). The format of Figure 6 was made similar to that of *Link and Cogger's* [1988] Figure 3 in order to facilitate a comparison of their results with ours, as described in more detail further ahead.

Figure 7 is the same as Figure 6 except that it was constructed adopting the Jacchia 77 model and height intervals of 10 km. The MSIS 86 and Jacchia 77 atmospheric models lead to close results regarding the height transition of the dominant quenching species. This fact can be observed in Figure 8, which shows the dominant quenching species in a given height range. Figure 8 was constructed from Figures 6 and 7 and from *Link and Cogger's* [1988] Figure 3. Notice that the atomic oxygen never becomes a dominant quenching species in the present result, as it does in the case of Link and Cogger. Such an ample dominance of atomic oxygen quenching, which occurs in the height range of 235-430 km, is owing to *Abreu et al.'s* [1986] large estimation $k_7=8\times10^{-12}$ cm^3 s^{-1} used by Link and Cogger in their Figure 3 which is about 1 order of magnitude larger than ours. Otherwise the results of Link and Cogger are consistent with the present ones. See for example in Figure 8 the N_2/e transition heights 320 km (dashed line), 290 km, and 309 km, respectively, for the Link and Cogger, Jacchia 77 and MSIS cases.

CONCLUSIONS

The nightime rocket experiment that has been carried out at Natal (geography 5.8°S, 35.2°W) on October 31, 1986, made it possible to estimate the rate coefficient k_7 of the $O(^1D)$ quenching by atomic oxygen.

Utilizing rocketborne data of the OI 630-nm emission rate and electron density, the MSIS 86 atmospheric neutral model and $f(^1D)$ equal to 1.1, the magnitude of k_7 was found to lie in the range between zero and 2.77×10^{-12} cm^3 s^{-1} and to have a mean value equal to 9.2×10^{-13} cm^3 s^{-1}.

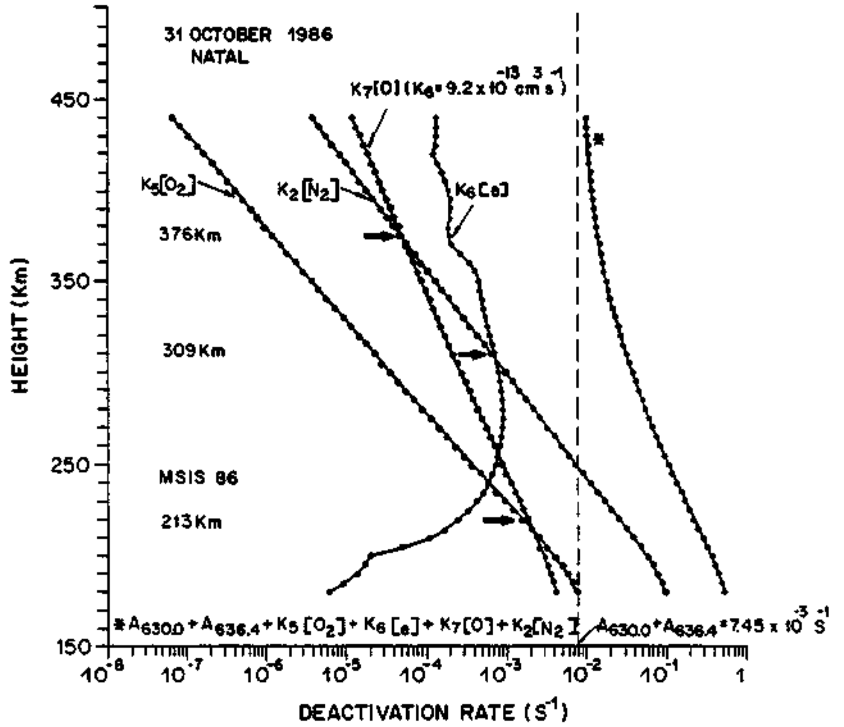

Fig. 6. Collisional deactivation rates of the O(^{1}D) in then octurnal F region calculated utilizing the MSIS 86 atmospheric model and measured electron density. The arrows indicate crossing heights of deactivation profiles. The heights shown on the left refer to the arrows. The vertical dashed line correspond to A_{1D}, the Einstein coefficient of the O(^{1}D) state. To the right of the dashed line is the overall deactivation rate which includes quenching and photoemissive deactivation.

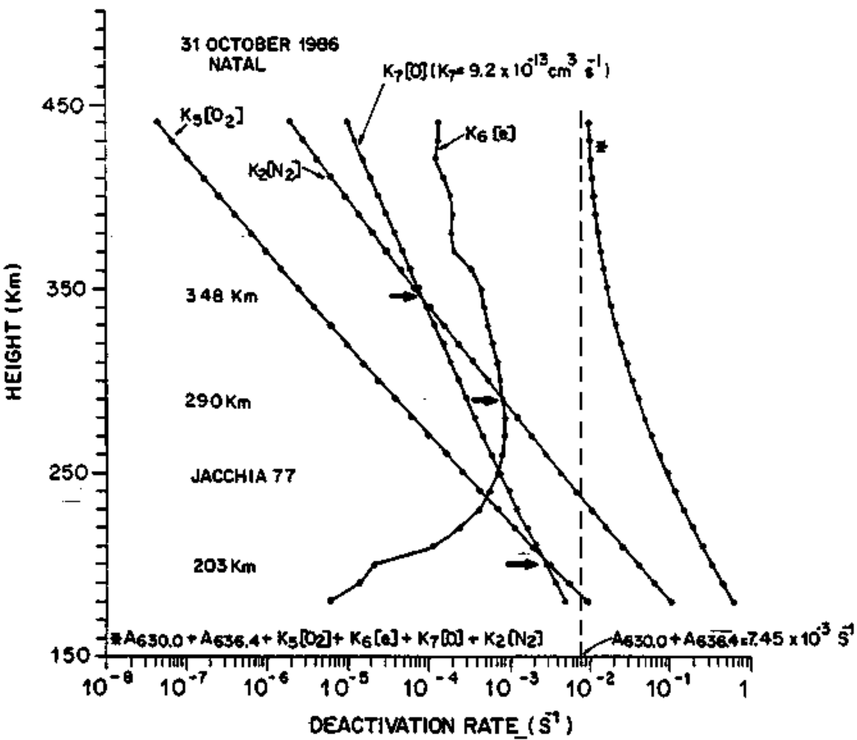

Fig. 7. Same as Figure 6 utilizing the Jacchia 77 atmospheric model.

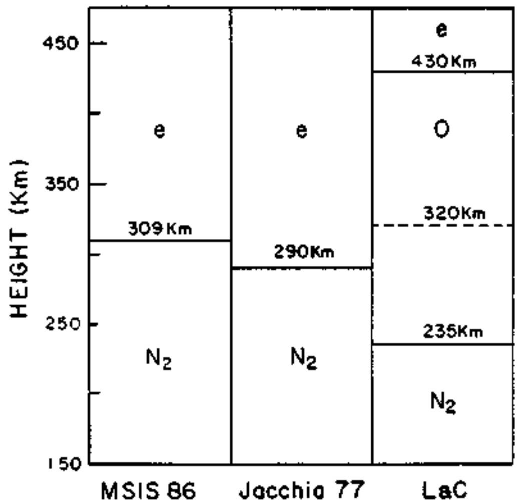

Fig. 8. Diagram showing the height regions for dominant quenching species according to the present results, using MSIS 86 and Jacchia 77 models, and to those of *Link and Cogger* [1988].

If f(^{1}D) is assumed to be equal to *Bates'* [1990, Table 13] Franck-Condon f(^{1}D), then the k_7 range and expected value turn out to be 1.03×10^{-12} cm^3 s^{-1} to 4.01×10^{-12} cm^3 s^{-1} and 2.55×10^{-12} cm^3 s^{-1}, respectively.

The result for k_7 in this work is in close agreement with those of *Abreu et al.* [1986] and *Yee et al.* [1990]. In the latter work, in particular, one of the potential curves resulted a calculated quenching rate of about 8.1×10^{-12} cm^3 s^{-1} , which, assuming a maximum error of a factor of 2 as cited in that paper, will result in a lower limit of 4.05×10^{-12} cm^3 s^{-1}. Considering the effects of the vibrational distribution of the O_2^+ ions (whose precise magnitude is not known), that limit is fairly close to the upper limit found here of 4.01×10^{-12} cm^3 s^{-1}.

The prevailing quenching species, as shown in Figure 8, are found to be N_2 in the altitude range of 150 km to 309 km or 150 km to 290 km depending upon whether MSIS 86 model [*Hedin*, 1987] or the Jacchia model [*Jacchia*, 1977] is adopted, respectively, with electrons inthe upper altitude range. Contrary to the finding of *Link and Cogger* [1988] the F region atomic oxygen did not turn out to be a major quenching species in the F region. The difference corresponds to the fact that our mean k_7 value is approximately an order of magnitude smaller than that adopted by Link and Cogger.

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M. A. Abdu, P. P. Batista, E. R. de Paula, P. Muralikrishna, Y. Sahai, J. H. A. Sobral, H. Takahashi and C. J. Zamlutti, Instituto Nacional de Pesquisas Espaciais, Caixa Postal 515, 12201-970, São José dos Campos, SP, Brazil

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