

DETERMINATION OF  $O_2(a^1\Delta_g)$  and  $O_2(b^1\Sigma^+g)$  YIELDS IN THE REACTION  $O + ClO \rightarrow Cl + O_2$ :  
IMPLICATIONS FOR PHOTOCHEMISTRY IN THE ATMOSPHERE OF VENUS

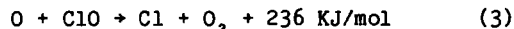
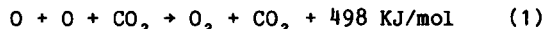
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**Abstract.** A discharge flow apparatus with chemiluminescence detector has been used to study the reaction  $O + ClO \rightarrow Cl + O_2^*$ , where  $O_2^* = O_2(a^1\Delta_g)$  or  $O_2(b^1\Sigma^+g)$ . The measured quantum yields for producing  $O_2(a^1\Delta_g)$  and  $O_2(b^1\Sigma^+g)$  in the above reaction are less than  $2.5 \times 10^{-2}$  and equal to  $(4.4 \pm 1.1) \times 10^{-4}$ , respectively. The observed  $O_2(a^1\Delta_g)$  airglow of Venus cannot be explained in the context of standard photochemistry using our experimental results and those reported in recent literature. The possibility of an alternative source of O atoms derived from  $SO_2$  photolysis in the mesosphere of Venus is suggested.

Introduction

The intense  $O_2(a^1\Delta_g)$  emission of Venus at  $1.27 \mu m$  was discovered by Connes et al. (1979), who estimated the dayglow and nightglow brightness to be 1.5 and 1.2 MR (1 Megarayleigh =  $1 \times 10^{12}$  photons  $cm^{-2} s^{-1}$ ), respectively. The authors also proposed that the most likely processes for producing  $O_2(a^1\Delta_g)$  on Venus are:



Detailed modeling by Yung and DeMore (1982) and Krasnopolsky and Parshev (1983) showed that, in order to explain the Venus observations, the quantum yields in reactions (1)-(3) must be close to unity.

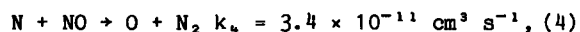
Reaction (1) has been studied by a number of workers (see recent review by Wayne, 1985). The quantum yields for singlet oxygen (both a and b states), as summarized in Table 3, are low. Reaction (2) was studied by Choo and Leu (1985b), who found no evidence for the production of excited  $O_2$  (see Table 3). In this article we shall report new experimental results on the quantum yields of singlet oxygen produced by reaction (3). Using the known efficiencies for producing  $O_2(a^1\Delta_g)$  in (1)-(3), we can make quantitative comparison of the modeled and observed airglow brightness of Venus. The results will be briefly discussed.

Experiment

The experimental technique used in this study has been described in detail in previous publi-

cations (Leu, 1984; Choo and Leu, 1985b). The production and detection of the singlet oxygen molecules,  $O_2(a^1\Delta_g)$  and  $O_2(b^1\Sigma^+g)$ , were carried out in a discharge flow apparatus with a chemiluminescence detector.

Oxygen atoms were produced in the side arm of the flow tube via the fast reaction (DeMore et al., 1985)



where the nitrogen atoms were generated in a microwave discharge by passing nitrogen gas through a quartz tube. Since the N atoms were slightly in excess, the final O atom concentration would be equal to that of NO, which was measured with a mass flowmeter.

ClO radicals were generated as follows: First, Cl atoms in the concentration range  $(5-10) \times 10^{13} \text{ cm}^{-3}$  were produced by passing a small amount of  $Cl_2$  in a helium carrier through a microwave discharge tube. Then, Cl atoms, in slight excess, were allowed to react with  $Cl_2O$  in a fast reaction leading to the production of ClO (DeMore et al., 1985)



The  $Cl_2O$  molecules used in this work were prepared as described in Leu (1984). The absolute concentration of  $Cl_2O$  was monitored by an optical absorption technique. The light source was a low pressure mercury lamp, which emits a strong line at 253.7 nm, and the adopted cross section for  $Cl_2O$  at this wavelength is  $2.01 \times 10^{-18} \text{ cm}^2$  (Lin, 1976; Molina and Molina, 1978). The detector was a photomultiplier equipped with an interference filter. By virtue of the stoichiometry of reaction (5), the final concentration of ClO must equal the initial concentration  $Cl_2O$ . Having prepared the ClO molecules in this manner, they were then introduced into the reaction cell via a movable Pyrex injector.

The observation of the singlet oxygen emissions was carried out using the chemiluminescence detection system. Radiation in the wavelength range 600-900 nm was resolved with a 1/4 m McPherson monochromator (Model 275) and registered by a Hamamatsu cooled photomultiplier tube (Model R943-02) in conjunction with a Keithley picoammeter (Model 480). Radiation in the wavelength 900-1700 nm was resolved with an Oriel grating monochromator (Model 7240) and detected with a liquid nitrogen cooled germanium detector (Applied Detector Corp. Model 403L). The signals were modulated with a 100 Hz chopper (Bulova) and a lock-in amplifier (EG & G Model 5804) was used for the phase sensitive detection. Emis-

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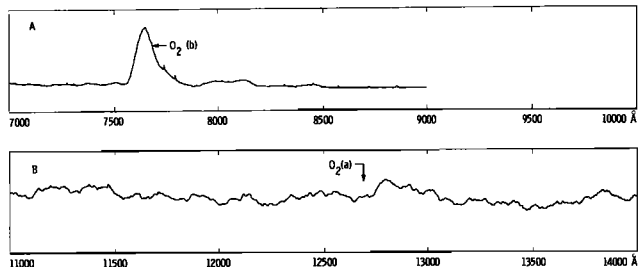


Fig. 1. Chemiluminescence spectra taken from the reaction of atomic oxygen with ClO radical (see text for detail). The  $O_2(b)$  emission at 7620 Å is clearly present. The  $O_2(a)$  emission at 12700 Å is absent.

sions from both singlet oxygen states were simultaneously recorded on a two-channel recorder. The calibration of these emissions was discussed previously (Choo and Leu, 1985b) and will not be repeated here.

Figure 1 shows the chemiluminescence data taken under the following conditions:  $[O] = [ClO] = 1.7 \times 10^{13} \text{ cm}^{-3}$  ( $[x]$  denotes the concentration of species  $x$ ); total pressure = 1.25 Torr; flow velocity = 3620  $\text{cm s}^{-1}$ ; and reaction time = 4.8 ms.  $O_2(b^1\Sigma_g^+)$  emission at 762 nm with a bandwidth of 10 nm was clearly detected. This result suggests that there were  $3.8 \times 10^9 \text{ cm}^{-3}$  of  $O_2$  in the  $b^1\Sigma_g^+$  state, produced by reaction (3).  $O_2(a^1\Delta_g)$  emission at 1270 nm was not detectable in the same experiment.  $O_2(a^1\Delta_g)$  concentration was estimated to be less than  $2 \times 10^{11} \text{ cm}^{-3}$ . The experimental data are summarized in Table 1. In order to derive the quantum yields of  $O_2(a^1\Delta_g)$  and  $O_2(b^1\Sigma_g^+)$ , a computer simulation was employed. The set of relevant chemical reactions is listed in Table 2. The rate of loss of  $O_2(b^1\Sigma_g^+)$  on the walls of the reaction cell and quenching by  $N_2$  has been measured using the same technique as reported here. The rates of loss of  $O_2(a^1\Delta_g)$  by quenching on the walls and by collisions with  $N_2$ , Cl, O, and ClO are very small (Wayne, 1985) and can be neglected in the computer simulation. The experimental conditions have been chosen so as to minimize interference from the reactions (1) and Cl

+  $ClO_2 \rightarrow Cl_2 + O_2$  (Choo and Leu, 1985b). The results of our analysis can be summarized as:  $k_a < 9 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ , and  $k_b = (1.6 \pm 0.4) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$  for the absolute rate constants for (3) to produce  $O_2(a^1\Delta_g)$  and  $O_2(b^1\Sigma_g^+)$ , respectively. The uncertainty represents one standard deviation error.

#### Discussion

The quantum yields for producing  $O_2(a^1\Delta_g)$  and  $O_2(b^1\Sigma_g^+)$  for reaction (3) are summarized in Table 3, which also includes results for other simple reactions capable of producing the singlet oxygen states. In general, the quantum yields are very small, ranging from less than  $10^{-4}$  to  $4 \times 10^{-2}$ .

According to Yung and DeMore (1982), the  $O_2(a^1\Delta_g)$  emissions due to (1), (2), and (3) could be as high as 0.72, 0.37, and 0.72 MR, respectively, adding up to a total of 1.8 MR, if the quantum yields for forming  $O_2(a^1\Delta_g)$  in the reactions were unity. However, using the current values for quantum yields, we obtain revised estimates of  $O_2(a^1\Delta_g)$  emission (including cascading from  $O_2(b^1\Sigma_g^+)$ ) due to (1), (2), and (3) as 0.029, 0.007, and 0.014 MR, respectively. The total amounts to 0.05 MR, considerably less than the observed 1.2–1.5 MR.

We now face a fundamental dilemma. Reaction (1) turns oxygen atoms into  $O_2$ . Reactions (2) and (3) constitute a catalytic cycle for converting odd oxygen into  $O_2$ . The ultimate source of O atoms in the upper atmosphere of Venus in the present model is  $CO_2$  photolysis, which proceeds at a mean rate of  $8 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ . This implies that the total rate of O-O bond formation cannot exceed  $4 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ . Therefore, if the quantum yield for producing the  $a^1\Delta_g$  state is  $q$  in each O-O bond forming reaction, the airglow would be less than  $4q$  MR. The recent laboratory results suggest that  $q$  is a few percent or less. Hence, the  $O_2(a^1\Delta_g)$  emission of Venus cannot arise from O-O bond forming reactions in which the O atoms are derived from  $CO_2$  dissociation. The simplicity of the argument outlined here suggests that our conclusion is largely independent of the details of the photochemical model.

One obvious possibility is that there might

Table I. Summary of  $O_2(b^1\Sigma_g^+)$  Measurements<sup>+</sup>

$[O]$ ( $\text{cm}^{-3}$ )	$[ClO]$ ( $\text{cm}^{-3}$ )	Reaction Time (ms)	$[O_2(b)]$ ( $\text{cm}^{-3}$ )	$k_b^*$ ( $\text{cm}^3 \text{ s}^{-1}$ )	Number of Experiments
1.5(13)	4.9(12)	3.0	1.0(9)	1.2(-14)	1
1.5(13)	1.6(13)	3.0	2.8(9)	1.3(-14)	1
1.6(13)	1.1(13)	4.8	3.4(9)	1.9(-14)	3
1.6(13)	1.6(13)	4.8	3.6(9)	1.6(-14)	2
1.6(13)	1.7(13)	4.8	3.8(9)	1.4(-14)	6
1.6(13)	1.9(13)	4.8	5.2(9)	2.1(-14)	1
Average Value $(1.6 \pm 0.4) \times (-14)^{**}$					

<sup>+</sup>The numbers a(b) should be read as  $a \times 10^{-b}$  in this table and Tables II and III.

\* Best fit of the  $O_2(b^1\Sigma_g^+)$  measurement.

\*\* One standard deviation.

Table II. Chemical scheme for computer simulation of the production of  $O_2(a^1\Delta_g)$  and  $O_2(b^1\Sigma^+_g)$  in the reaction  $O + ClO \rightarrow Cl + O_2$ 

Reactions	Rate Constant ( $cm^3 s^{-1}$ )	References
$O + ClO \rightarrow Cl + O_2$	3.6(-11)	Leu
$Cl + O_2(a)$	<9.0(-13)	This work
$Cl + O_2(b)$	1.6(-14)	"
$O_2(a) + wall \rightarrow O_2$	<1.0*	Choo and Leu (b)
$O_2(a) + N_2 \rightarrow O_2 + N_2$	1.0(-19)	Wayne
$O_2(a) + Cl \rightarrow O_2 + Cl$	1.0(-16)	**
$O_2(a) + O \rightarrow O_2 + O$	1.0(-16)	**
$O_2(a) + ClO \rightarrow O_2 + ClO$	1.0(-16)	**
$O_2(b) + wall \rightarrow O_2$	80.0*	Choo and Leu (a)
$O_2(b) + N_2 \rightarrow O_2 + N_2$	1.7(-15)	"
$O_2(b) + Cl \rightarrow O_2 + Cl$	1.0(-13)	**
$O_2(b) + O \rightarrow O_2 + O$	1.0(-13)	**
$O_2(b) + ClO \rightarrow O_2 + ClO$	1.0(-13)	**

\*in units of  $s^{-1}$ .

\*\*Estimated based on analogous reactions; see the review by Wayne (1985).

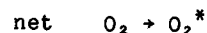
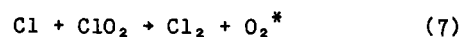
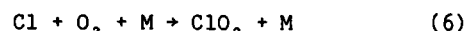
have been a calibration error in the observations. A discussion with one of the authors (Traub, 1987, private communication) led to a critical re-examination of the data analysis procedure used in Connes et al.'s (1979) paper. It was concluded that calibration errors could have been at most a factor of 2, since two independent methods, based on the terrestrial airglow and the Venus continuum brightness were used, and both methods gave essentially the same result.

We can speculate on other explanations. The crucial clue is the source of O atoms. As was first pointed out by Winick and Stewart (1980), photolysis of  $SO_2$  is a major source of O atoms in the stratosphere of Venus. Indeed, according to the models of Winick and Stewart (1980), and Yung and DeMore (1982), the photolysis rate of  $SO_2$  on Venus is about  $2 \times 10^{13} cm^{-2} s^{-1}$  and is considerably higher than that of  $CO_2$ . However, most of the photolysis of  $SO_2$  occurs in the lower part of the stratosphere, just above the cloud tops (-60 km). Any  $O_2(a^1\Delta_g)$  produced in this region would be effectively quenched, and could not contribute to the observed emissions under "normal" circumstances.

Consider now an unusual event, an episodic injection of  $SO_2$  into the upper atmosphere of Venus. We shall leave the cause of this event unspecified, although volcanism is a possibility (Esposito, 1984). The presence of large quantities of  $SO_2$  in the upper stratosphere (above 80 km), with mixing ratio equivalent to  $10^{-5}$ , would lead to rapid photolysis and production of oxygen atoms. Recombination of these atoms either by (1) or the catalytic cycle (2) and (3) would yield a source of  $O_2(a^1\Delta_g)$ . Detailed modeling of this event appears difficult since the  $O_2(a^1\Delta_g)$  airglow observations were carried out in 1975, before there were any quantitative data on  $SO_2$  (Pioneer-Venus started collecting

data in 1978). Since the normal  $SO_2$  mixing ratio in the stratosphere is of the order of  $10^{-7}$  or less, and enhancement of  $SO_2$  concentration by two orders of magnitude is an unlikely event.

All the mechanisms we have discussed produced  $O_2(a^1\Delta_g)$  via the formation of a new O-O bond and hence they are limited by the source of oxygen atoms. However, we would like to point out the following possibility:



where  $O_2^* = O_2(a^1\Delta_g)$  or  $O_2(b^1\Sigma^+_g)$ . In this mechanism no new O-O bonds are formed. Chlorine serves as a catalyst for converting solar energy in the visible into chemical energy. Using the model of Yung and DeMore (1982) and the quantum yields listed in Table 3, we estimate an airglow brightness of 0.2 MR due to this mechanism. This is clearly insufficient to explain the observations.

### Conclusions

A discharge flow apparatus with a chemiluminescence detector has been used to determine the quantum yields of  $O_2(a^1\Delta_g)$  and  $O_2(b^1\Sigma^+_g)$  in the reaction  $O + ClO \rightarrow Cl + O_2$ . The results are summarized in Tables 2 and 3. Application of these results to explain the airglow brightness of Venus reveals a fundamental difficulty with a "normal" photochemical model. There may be another source of oxygen atoms in the upper atmosphere of Venus derived from  $SO_2$  photolysis.

Table III. List of the relevant reactions that produce  $O_2(a^1\Delta_g)$  and  $O_2(b^1\Sigma^+_g)$  in the atmosphere of Venus and their quantum yields

Reactions	Quantum Yield*		References
	$O_2(a)$	$O_2(b)$	
$O + O + M \rightarrow O_2 + M$	4(-2)	2(-2)	Wraight
		3(-2)	Ogryzlo et al.
		4(-5)	Young and Black
$Cl + O_3 \rightarrow ClO + O_2$	<2(-2)	<5(-4)	Choo and Leu (b)
$O + ClO \rightarrow Cl + O_2$	<2.5(-2)	4.4(-4)	This work
$Cl + ClO_2 \rightarrow Cl_2 + O_2$	1.4(-2)	6(-3)	Choo and Leu (b)
$Cl + HO_2 \rightarrow HCl + O_2$		<5(-4)	Keyser et al.
$H + HO_2 \rightarrow H_2 + O_2$	1.5(-2)		Washida et al.
		2.8(-4)	Hislop and Wayne
		<1(-2)	Keyser et al.
$O + HO_2 \rightarrow OH + O_2$		<8(-3)	Keyser et al.

\*Defined as the rate coefficient for the branch divided by the total rate coefficient.

"Normal"  $SO_2$  abundance in the mesosphere would be too low. However, the atmosphere of Venus might have been strongly perturbed by a massive injection of  $SO_2$  in 1975.

It is important that our laboratory kinetics-chemiluminescence results be confirmed using an independent experimental technique. Also, the  $O_2(a^1\Delta_g)$  emission from Venus has been observed only once, and these observations should be repeated to establish the magnitude and nature of possible variations, along with the simultaneous observation of other chemical species such as  $CO$ ,  $H_2O$ ,  $HCl$ ,  $HF$ ,  $O_2$ , and  $SO_2$ .

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