

Preliminary Note

On the excitation of the night airglow on Earth, Venus and Mars

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The absorption of solar radiation by O_2 in the Earth's atmosphere produces a layer of oxygen atoms whose maximum concentration lies at an altitude of about 97 km [1]. The recombination of these oxygen atoms results in the production of a night airglow of about 1 kilorayleigh in the wavelength range 250 - 500 nm. In 1941 Dufay [2] proposed that the airglow originates from the $A^3\Sigma_u^+$ state of O_2 . This was confirmed by the absorption measurements of Herzberg [3] and the emission is consequently referred to as the Herzberg I bands ($O_2(A^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-)$). Subsequent workers [4 - 6] have shown that most of the emission comes from the third to the seventh vibrational levels of this state with a maximum from the fifth level.

More recently Krasnopolsky *et al.* [7] obtained the night airglow spectrum of Venus. The emission was found to originate at about the same altitude as the Earth's night airglow but with an intensity about seven times as great. The simple sequence of 11 bands lying between 350 and 700 nm clearly did not belong to the Herzberg I system and were subsequently identified by Lawrence *et al.* [8] as an emission exclusively from the zeroth vibrational level of the $c^1\Sigma_u^-$ state of O_2 to its ground state (called Herzberg II bands) [9]. The intriguing question raised by a comparison of the night airglows on these two planets is why they should originate from two different states of O_2 when they are undoubtedly both formed by the slow recombination of oxygen atoms on the dark side of each planet.

Noting the presence of CO_2 in the atmosphere of Venus, Lawrence *et al.* [8] prepared atomic oxygen in a large excess of CO_2 and observed that the normal Herzberg I emission bands disappeared and were replaced by $\nu' = 0$ Herzberg II bands. They therefore proposed that the change could be attributed to "the very special role that carbon dioxide plays as a third body in the Venus night airglow". An alternative explanation was proposed by Krasnopolsky *et al.* [10]. They pointed out that no night airglow has been detected on Mars which also has an atmosphere predominantly composed of CO_2 but with a relative O_2 concentration which is at least 10^8 times larger than that on Venus. Consequently they proposed that "it would therefore be

worthwhile to test the hypothesis that luminescence in the band system under discussion is absent on Mars (and also on Earth) because of suppression by O_2 " [10].

The experiments described in this paper were an attempt to determine whether the appearance of the Herzberg II bands on Venus can be attributed to the lack of molecular oxygen in that atmosphere (as proposed by Krasnopolsky *et al.* [10]) rather than the presence of CO_2 (as proposed by Lawrence *et al.* [8]).

1. Experiments and results

Oxygen atoms were formed by passing a mixture of O_2 and Ar through a 100 W 2450 MHz microwave discharge. Ultrahigh purity oxygen was used without further purification; the argon was passed over titanium sponge at $850^\circ C$ to remove the nitrogen impurity. The afterglow was observed 20 cm downstream from the discharge in a 1 l bulb coated internally with aluminium, fitted with light traps and a 2 cm sapphire window. The emission spectra were recorded with a Bausch and Lomb grating monochromator and an RCA 1P28 photomultiplier.

In Fig. 1 the uppermost curve shows a typical emission spectrum obtained when a stream containing 1.0% O_2 in Ar is passed through the discharge. Such spectra have been recorded by a number of earlier workers [11 - 13]. Almost all the bands can be assigned to the Herzberg I system. The effect of decreasing the amount of O_2 in the stream at constant total

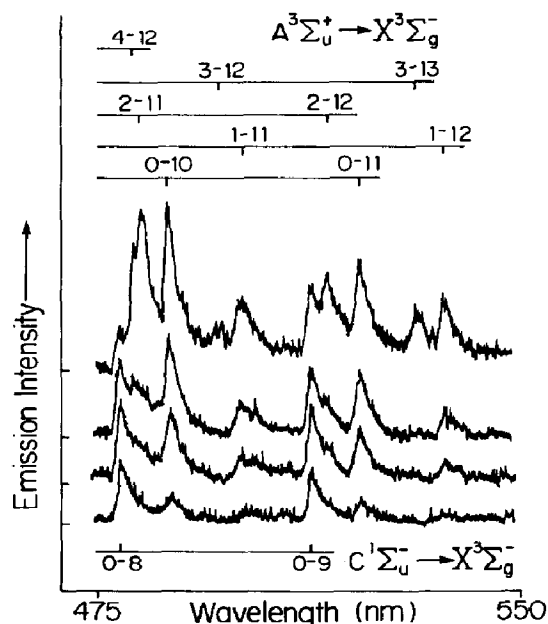


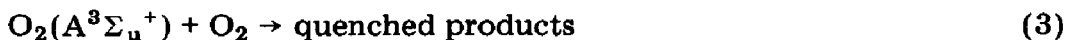
Fig. 1. Argon-oxygen afterglow spectrum between 475 and 550 nm as a function of the $[Ar]/[O_2]$ ratio. Uppermost curve, $[Ar]/[O_2] \approx 10^{-2}$; lower curves, $Ar/O_2 \approx 2 \times 10^{-4}$. Note that the curves have been displaced along the vertical axis.

pressure is shown in the lower curves of Fig. 1. It can be seen that decreasing the $O_2:Ar$ ratio has two effects on the spectrum. Emission from lower vibrational levels of the $O_2(^3\Sigma_u^+)$ state increases relative to the emission from higher levels and, more significantly, emission from the $v = 0$ level of the $O_2(c^1\Sigma_u^-)$ state becomes more significant. At the lowest O_2 flow recorded the Herzberg II bands dominate the emission spectrum.

These spectra make it clear that CO_2 is not essential for the production of a spectrum which is predominantly made up of the "Herzberg II bands"[†]. One is tempted to conclude that emission from $c^1\Sigma_u^-$ is quenched by O_2 as suggested by Krasnopolsky *et al.* [10]. However, it would appear that the explanation is not that simple because both the Herzberg I and Herzberg II bands are quenched by O_2 . When O_2 is added to the stream after the discharge there is no significant change in the ratio of the Herzberg I and II emission intensities although emission from both excited states decreases. We are thus led to the conclusion that it is the decreasing oxygen atom concentration that is responsible for the increasing emission from $O_2(c^1\Sigma_u^-)$ relative to $O_2(A^3\Sigma_u^+)$.

This was verified by changing the oxygen atom concentration, keeping the Ar and O_2 flows constant. The results show that, in contrast to the Herzberg I bands which are second order in $[O]$, the Herzberg II bands are first order in $[O]$. This can only be true if the $O_2(^1\Sigma_u^-)$ state is quenched by oxygen atoms.

If oxygen atoms are the dominant quenching species for the $O_2(c^1\Sigma_u^-)$ then the simultaneous efficient quenching by O_2 can only be explained if O_2 quenches a precursor of this state. We are therefore led to the following mechanism which is capable of explaining the observations in our laboratory and in the night airglow on Earth and Venus:



Assuming that the radiative processes are very much slower than the collisional processes and that $k_3[O_2] \gg k_4[M]$, standard steady state assumptions yield the following emission intensities:

$$I(\text{Herzberg I}) = \frac{k_1 k_2}{k_3} [O]^2 \frac{[M]}{[O_2]} \quad (7)$$

[†]T. G. Slanger has also obtained this result [14].

$$I(\text{Herzberg II}) = \frac{k_1 k_4 k_5}{k_3 k_6} [\text{O}] \frac{[\text{M}]^2}{[\text{O}_2]} \quad (8)$$

$$\frac{I(\text{Herzberg II})}{I(\text{Herzberg I})} = \frac{k_4 k_5}{k_2 k_6} \frac{[\text{M}]}{[\text{O}]} \quad (9)$$

Equation (7) predicts that the Herzberg I band intensities vary as the square of the oxygen atom concentration as shown by previous workers [13, 15]; however, it also predicts that they should be proportional to $[\text{M}]/[\text{O}_2]$. McNeal and Durana [13] would not have observed this dependence because their kinetic measurements were carried out in pure O_2 . Young and Black [15] reported no dependence on M in their experiments. We suspect that the large observation bulb used by these workers resulted in the production of larger amounts of O_2 at higher pressures so that the ratio $[\text{M}]/[\text{O}_2]$ remained constant with increasing pressure, masking the true dependence on M.

We have experimentally verified that the dependence of the ratio of the Herzberg I and Herzberg II bands is independent of the O_2 concentration and proportional to the ratio $[\text{M}]/[\text{O}]$ as required by eqn. (9).

We are now in a position to reassess answers to the questions raised by the observation of only Herzberg II bands in the night airglow on Venus, only Herzberg I bands in Earth's atmosphere and inability to detect any night airglow on Mars.

We begin by repeating that the ratio of the emission intensities from the $\text{A}^3\Sigma_u^+$ state and the $\text{c}^1\Sigma_u^-$ state are independent of the O_2 concentration so that this species itself cannot be responsible for the change in emitting state. The transition from Herzberg I bands to Herzberg II bands can, however, be accomplished by a change in the ratio $[\text{M}]/[\text{O}]$. As illustrated by the last two entries in Table 1, when the ratio $[\text{M}]/[\text{O}]$ is about 500 the Herzberg I bands are dominant. When the ratio is 5×10^3 or greater the Herzberg II bands dominate. Clearly, on Earth, where the $[\text{M}]/[\text{O}]$ ratio is only 25, the Herzberg II bands will be virtually absent. On Venus, with an $[\text{M}]/[\text{O}]$ ratio of 3.3×10^5 the emission would be predominantly Herzberg II bands even if the atmosphere were principally argon. It is worth noting, however, that CO_2 is about 100 times as effective as argon at bringing about this change in emitting states [19] and therefore a smaller $[\text{M}]/[\text{O}]$ ratio is necessary to bring out the Herzberg II bands on a planet like Venus or Mars. We should like to emphasize that all our evidence points to the greater effectiveness of CO_2 as M in reaction (4) but not as a unique third body in the termolecular recombination process. To reinforce this view we have tested the effect of a number of other foreign gases on this system [19] and find that molecules such as CCl_4 and some Freons which possess vibrational frequencies matching the vibrational spacings in the $\text{A}^3\Sigma_u^+$, $\text{C}^3\Delta_u$ and $\text{c}^1\Sigma_u^-$ states are almost equally effective.

Now let us consider why the Martian night airglow is at least two orders of magnitude weaker than that on Venus. In view of the large $[\text{M}]/[\text{O}]$ ratio in the emitting layer (see Table 1) there is little doubt that the emission

TABLE 1

| | [M] ^a | [O ₂] ^a | [O] ^a | [M]/[O] | Reference |
|---------------------------------------|----------------------|--------------------------------|------------------------|-----------------------|-----------|
| Earth (95 km) | 10 ¹³ | 2 × 10 ¹² | 4 × 10 ¹¹ | 25 | 16 |
| Venus (92 km) | 10 ¹⁶ | 5 × 10 ¹⁰ | 3 × 10 ¹⁰ | 3.3 × 10 ⁵ | 17 |
| Mars (35 km) | 6 × 10 ¹⁵ | 5 × 10 ¹² | 3 × 10 ⁹ | 2 × 10 ⁶ | 18 |
| Laboratory (Herzberg I) (15 Torr) | 5 × 10 ¹⁷ | 5 × 10 ¹⁵ | 1 × 10 ¹⁵ | 500 | this work |
| Laboratory (Herzberg II) (19 Torr) | 6 × 10 ¹⁷ | 8 × 10 ¹³ | 1.2 × 10 ¹⁴ | 5 × 10 ³ | this work |

^aUnits are molecules cm⁻³.

would be Herzberg II bands. From eqn. (8) it follows that the ratio of the intensities of the Martian and Venusian airglows is given by

$$\frac{I_{\text{Mars}}}{I_{\text{Venus}}} = \frac{[\text{O}_2]_{\text{Venus}}}{[\text{O}_2]_{\text{Mars}}} \frac{[\text{O}]_{\text{Mars}}}{[\text{O}]_{\text{Venus}}} \frac{[\text{M}]^2_{\text{Mars}}}{[\text{M}]^2_{\text{Venus}}}$$

Using the data in Table 1

$$\frac{I_{\text{Mars}}}{I_{\text{Venus}}} = (10^{-2})(10^{-1})(0.36) = 3.6 \times 10^{-4}$$

This is consistent with the inability of the Mars 5 satellite to detect the Martian afterglow [20]. It is also interesting to observe that this is mostly attributable to the higher O₂ but lower O concentration on Mars. However, since the estimate is based on calculated rather than measured concentrations on Venus and Mars it should be viewed only as a tentative estimate.

Acknowledgments

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