Journal of Photochemistry, 12 (1980) 179 - 183

Preliminary Note

On the excitation of oxygen emissions in the airglow of the terrestrial planets

E. J. LLEWELLYN and B. H. SOLHEIM

Institute of Space and Atmospheric Studies, University of Saskatchewan, Saskatoon S7N OWO (Canada)

G. WITT and J. STEGMAN

Department of Meteorology, University of Stockholm, Arrhenius Laboratory, S-106 91 Stockholm (Sweden)

R. G. H. GREER

Department of Pure and Applied Physics, Queen's University, Belfast BT7 1NN (Northern Ireland)

(Received May 16, 1979)

The recombination of oxygen atoms in the Earth's atmosphere leads to airglow emissions from both molecular and atomic oxygen. However, the precise details of the excitation mechanisms for these emissions remain uncertain and, with the recent observation of the Venus night airglow spectrum [1, 2], the need to clarify the various excitation processes has become apparent [3, 4]. The excitation of the atomic oxygen green line (OI, ^1S–^1D) was originally proposed to occur through the Chapman mechanism [5, 6], *i.e.* through the three-body recombination of oxygen atoms with atomic oxygen acting as the third body.

However, following laboratory measurements [7] of the quenching of the $O(^1S)$ state, Barth [8] proposed that an indirect process (or two-step mechanism) was more appropriate. He suggested the following kinetic scheme, now known as the Barth mechanism:

$$O + O + M \rightarrow O_2^* + M \tag{1}$$

$$O_2^* + O \rightarrow O_2 + O(^1S) \tag{2}$$

$$O_2^* + M,O_2,O \rightarrow \text{quenched products} \tag{3}$$

$$O(^1S) \rightarrow O(^1D,^3P) + h\nu \tag{4}$$

$$O(^1S) + O,O_2M \rightarrow \text{quenched products} \tag{5}$$

$$O_2^* \rightarrow O_2 + h\nu \tag{6}$$

In proposing this scheme Barth did not identify the excited intermediate O_2^*, although he did suggest that it could be either the $c^1\Sigma_u^-$ state or the

$C^3\Delta_u$ state. These excited states are the sources of the Herzberg II and Herzberg III bands respectively, and emission from these states has been identified in the Venus airglow [2]. Only the Chamberlain bands ($C^3\Delta_u \rightarrow a^1\Delta_g$) have been identified in the Earth's airglow [9, 10]. Since the Barth mechanism was first proposed there has been a controversy as to the exact nature of the excitation mechanism [11], although a recent laboratory measurement of the appropriate rate constant [12] has indicated the validity of the transfer mechanism. In considering the implications of their measurements for the airglow Slanger and Black [13] proposed that the excited intermediate is probably the $O_2(A^3\Sigma_u^+)$ state, the source of the Herzberg I bands in the Earth's airglow. These authors do suggest that other states could be important but do not consider either the $c^1\Sigma_u^-$ state or the $C^3\Delta_u$ state as likely precursors.

Recently, new rocket observations of the oxygen green line and of molecular oxygen features in the airglow have been reported by Witt *et al.* [14] and by Thomas *et al.* [15]. These investigators have independently shown that the two-step process is more appropriate to the interpretation of their measurements, but, in view of the different identification by these two groups of the intermediate state, $O_2(c^1\Sigma_u^-)$ and $O_2(A^3\Sigma_u^+)$ respectively, there has remained some uncertainty. However, Solheim and Llewellyn [16] have considered the implications of a two-step process for the auroral excitation of the oxygen green line and have concluded that the identification of the intermediate as $O_2(c^1\Sigma_u^-)$ is not inconsistent with the apparent absence of the Herzberg I bands in the aurora. It should also be noted that independent theoretical considerations [17] for both the Chapman mechanism and the Barth mechanism support the excitation of the green line through a transfer mechanism but do not explicitly identify the precursor.

In a recent publication Kenner *et al.* [18] have reported preliminary measurements of the Herzberg I and II bands in a flow system. These authors concluded that the $O_2(c^1\Sigma_u^-)$ state is populated by transfer from the $O_2(A^3\Sigma_u^+)$ state and that this is consistent with observations of the airglows of Earth, Venus and Mars. In the present note we consider this matter in more detail and we suggest that the measurements themselves comment on the identity of the intermediate state in the Barth mechanism for the excitation of the green line.

Initially we will assume that the intermediate state is $O_2(A^3\Sigma_u^+)$, in agreement with the proposal of Slanger and Black [13]. For steady state conditions and where quenching dominates, the emission intensity of the Herzberg I bands in the flow tube [18] is given by

$$I\,(\text{Herzberg I}) = \frac{k_1 k(A^3\Sigma_u^+)_6[O]^2[M]}{k_{3,O}[O] + k_{3,O_2}[O_2] + k_{3,M}[M]} \tag{7}$$

Also, if $k_{3,M}[M] \ll k_{3,O_2}[O_2]$, the equation may be further simplified to

$$I\,(\text{Herzberg I}) = \frac{k_1 k(A^3\Sigma_u^+)_6[O]^2[M]}{k_{3,O}[O] + k_{3,O_2}[O_2]} \tag{8}$$

The limiting cases for eqn. (8) are determined by the denominator which may tend to either $k_{3,O}[O]$ or $k_{3,O_2}[O_2]$. For $k_{3,O_2}[O_2] \gg k_{3,O}[O]$ the Herzberg I intensity dependence would be proportional to $[O]^2[M]/[O_2]$, similar to that proposed by Kenner *et al.* [18]. If $k_{3,O_2}[O_2] \ll k_{3,O}[O]$ then the intensity of the Herzberg I bands is proportional to only the first power of the atomic oxygen concentration which is certainly contrary to observation [18 - 20]. Hence, from the flow tube concentrations used by Kenner *et al.* [18] we may estimate that $k_{3,O_2} \geqslant k_{3,O}$, or that the rate coefficient for the $O_2(A^3\Sigma_u^+)$ quenching by atomic oxygen is less than 3×10^{-13} cm^3 s^{-1} [20]. From the analysis of the atomic oxygen green line in the airglow Slanger and Black [13] concluded that the transfer (or quenching) coefficient for $O_2(A^3\Sigma_u^+)$ by atomic oxygen must be at least 2.6×10^{-11} cm^3 s^{-1}. As this value is significantly larger than that just derived there is support for the suggestion that the $O_2(A^3\Sigma_u^+)$ state is not the precursor for the oxygen green line. We would further suggest that the original assumption which permitted us to neglect the term $k_{3,M}[M]$ in eqn. (7) is incorrect, so that the equation should be rewritten as

$$I\,(\text{Herzberg I}) = \frac{k_1 k(A^3\Sigma_u^+)_6[O]^2[M]}{k_{3,M}[M]} \tag{9}$$

or[

$$I\,(\text{Herzberg I}) = \frac{k_1 k(A^3\Sigma_u^+)_6[O]^2}{k_{3,M}} \tag{10}$$

Equation (10) is consistent with the expression derived by Young and Black [20] from laboratory observations which did not show a third-body dependence.

Equation (10) does not in fact require that the $O_2(A^3\Sigma_u^+)$ state is formed directly in the recombination and it could be populated through a transfer process similar to that postulated by Kenner *et al.* [18] for the $O_2(c^1\Sigma_u^-)$ state. This possibility has recently been proposed by Llewellyn *et al.* [21] who have shown that measurements of the Herzberg I bands in the Earth's airglow are consistent with a transfer process through O_2 and N_2 from some intermediate state. This intermediate state has not been identified, although the $O_2(C^3\Delta_u)$ state has been postulated. The kinetic scheme appropriate to the Llewellyn *et al.* [21] measurements is

$$O + O + M \rightarrow O_2^{**} + M \tag{11}$$

$$O_2^{**} + M,O_2,O \rightarrow \text{quenched products} \tag{12}$$

$$O_2^{**} + O_2 \rightarrow O_2(A^3\Sigma_u^+) + O_2 \tag{13}$$

$$O_2(A^3\Sigma_u^+) + O,O_2,M \rightarrow \text{quenched products} \tag{14}$$

Again for steady state conditions and dominant quenching, the emission intensity of the Herzberg I bands is given by

$$I\,(\text{Herzberg I}) = \frac{k(A^3\Sigma_u^+)_6[O]^2[M]}{k_{12,M}[M] + k_{12,O_2}[O_2] + k_{12,O}[O]} \times$$
$$\times \frac{k_{13}[O_2]}{k_{14,M}[M] + k_{14,O_2}[O_2] + k_{14,O}[O]} \tag{15}$$

If $k_{12,M}[M]$ and $k_{14,O_2}[O_2]$ are the controlling terms in the first and second denominators, this expression reduces to eqn. (10).

If it is assumed that the $O_2(c^1\Sigma_u^-)$ state is formed directly in the three-body recombination and is quenched predominantly by oxygen atoms, the intensity of the Herzberg II bands under steady state conditions is given by

$$I\,(\text{Herzberg II}) = \frac{k_1 k(c^1\Sigma_u^-)_6[O]^2[M]}{k_{3,O}[O]} \tag{16}$$

which is first order in [O] as required by the reported observations [18]. Thus the intensity ratio of the Herzberg II/Herzberg I bands in the flow tube is proportional to [M]/[O], which is again in agreement with experimental observations [18]. The rapid quenching of the $O_2(c^1\Sigma_u^-)$ state by oxygen atoms can easily satisfy the oxygen green line excitation required by the observations reported in refs. 14 and 15; consequently there is laboratory evidence to identify the $O_2(c^1\Sigma_u^-)$ state as the precursor in the Barth mechanism.

The excitation schemes we propose would also support the Herzberg II/Herzberg I intensity ratio derived by Kenner *et al.* [18] for the planetary airglows. However, it should be noted that care must be taken in the interpretation of such a ratio for, if quenching of the $O_2(A^3\Sigma_u^+)$ state by CO_2 [22] is dominant in the atmosphere of Venus, eqn. (15) would indicate a reduction of the Herzberg I emission due to both an absence of O_2 and the presence of CO_2. For the Martian airglow the problem is even more complicated as the large $[O_2]/[O]$ ratio could mean that the predominant loss of the $O_2(c^1\Sigma_u^-)$ state is through O_2 and that no Herzberg II emission would be expected. This idea has recently been developed by Greer *et al.* [23] who have shown that such a quenching mechanism could lead to the oxygen atmospheric bands, as suggested by earlier laboratory studies [19, 24]. In contrast, the oxygen atmospheric bands would not be a conspicuous feature of the Martian airglow as $O_2(b^1\Sigma_g^+)$ is efficiently quenched by CO_2 [25, 26].

It is apparent that, although the exact nature of the excitation paths for the molecular oxygen emissions in the atmospheres of Earth, Venus and Mars remain uncertain, there are strong reasons for suggesting that transfer processes are important. This of course does not explain why certain molecular states are preferentially populated in the recombination of atomic oxygen.

Acknowledgments

This work has been supported through Grants-in-Aid from the National Research Council of Canada, contracts from the Swedish Board for Space Activities and by the International Institute of Meteorology in Stockholm.

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