SINGLET OXYGEN AIRGLOW[†]

R. P. WAYNE

Physical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ (Gt. Britain)

Summary

This survey of excitation processes for singlet O_2 in planetary atmospheres is intended to provide an introduction to the following papers in which laboratory investigations and field measurements are discussed in more detail. The three singlet states, $a\,^1\Delta_g$, $b\,^1\Sigma_g^+$ and $c\,^1\Sigma_u^-$, contribute to features in the airglows of Venus, Earth and Mars, the most intense feature being in each case the dayglow of the $O_2(a\,^1\Delta_g \rightarrow X\,^3\Sigma_g^-)$ "IR Atmospheric Band". O_3 photolysis is the daytime source of $O_2(^1\Delta_g)$ on Earth and Mars, but is unlikely to be on Venus. Some remaining problems about the O_3 photolytic source are reviewed, and possible excitation mechanisms on Venus are considered. $O_2(b\,^1\Sigma_g^+)$ is excited during the day in the terrestrial atmosphere by a combination of resonance scattering and of energy transfer from $O(^1D)$ to O_2. The state is unimportant on either Venus or Mars because of its sensitivity to quenching by CO_2, the major atmospheric constituent.

Nightglow emissions from $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g^+)$ are much harder to explain than the daytime phenomena, because they must be excited from chemical energy stored in species, such as H, O or O_3, that persist at night. Of the many mechanisms that have been proposed, none has been substantiated explicitly by laboratory experiments, and the hypothetical sources are frequently judged by their ability to match atmospheric measurements of airglow both for absolute intensity and for altitude profile. We consider here the additional factor of the *plausibility* of the mechanisms.

1. Introduction

In spite of the long radiative lifetime of the transition, the most intense molecular feature in the Earth's airglow is the $a\,^1\Delta_g \rightarrow X\,^3\Sigma_g^-$ "IR Atmospheric Band". Other airglow bands that involve singlet states of O_2 include the $b\,^1\Sigma_g^+ \rightarrow X\,^3\Sigma_g^-$ "Atmospheric Band", the $b\,^1\Sigma_g^+ \rightarrow a\,^1\Delta_g$ "Noxon" system and

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the $c\,^1\Sigma_u^- \to X\,^3\Sigma_g^-$ "Herzberg II" system. The IR Atmospheric Band is present in the airglow of both Venus and Mars, and the Herzberg II bands are an important component of the Venusian airglow. It is the purpose of this review to survey possible mechanisms by which the singlet species may become excited in the planetary atmospheres, in order to provide an introduction to the more detailed subsequent contributions on airglow observations and excitation mechanisms. Our approach will be first to consider briefly some of the results of atmospheric studies, and then to examine what laboratory experiments have to tell us about possible routes to excitation. Processes involving charged species are excluded from this survey, and auroral atmospheric emissions are thus generally omitted from consideration. Figure 1 shows some states of O_2 [1] and Fig. 2 identifies the optical transitions between them.
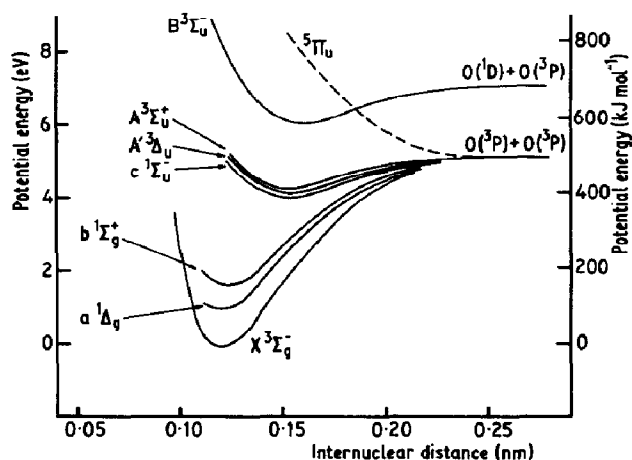
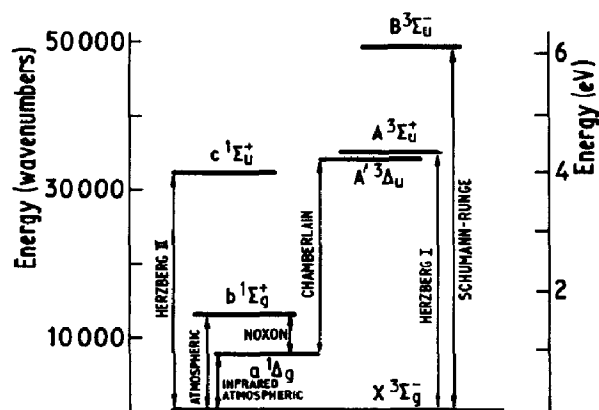Fig. 1. Some of the low-lying states of O_2. (Data from Krupenie [1].)

Fig. 2. Nomenclature for some of the optical transitions in O_2.

2. Singlet O_2 in planetary airglows

Ground-based observations of the IR Atmospheric system on Earth were confined initially [2 - 4] to the (0, 1) band at λ = 1.58 μm because of atmospheric reabsorption of the (0, 0) band. Aircraft- [5 - 7], balloon- [8] and rocket-borne [9] instruments allow measurements of the more intense (0, 0) transition at λ = 1.27 μm. Concentration–altitude profiles are most conveniently derived from rocket measurements. Intensity variations at twilight [5, 8] or, more spectacularly, in eclipses [6, 7] can assist in the elucidation of excitation and quenching mechanisms. Peak daytime concentrations of $O_2(^1\Delta_g)$, determined by rocket photometry, are typically [10, 11] 2×10^{10} molecules cm^{-3} at 50 - 60 km altitude, and the concentrations drop rapidly after the sun falls below the horizon or is eclipsed. Emission continues at night, albeit with much less intensity than in the dayglow. Gush and Buijs [12] first detected the IR Atmospheric Band in the Earth's nightglow with a balloon-borne Michelson interferometric instrument, and rocket photometer measurements have been described subsequently [13, 14].

The IR Atmospheric Band at λ = 1.27 μm is observed in the airglow of both Mars [15, 16] and Venus [17]. Measurements have been carried out at Mount Hopkins Observatory using a 1.5 m reflector with three Fabry–Perot etalons in series, and at Mount Palomar using the 5 m telescope with a Fourier transform spectrometer. The high spectral resolution that was attained permits individual rotational lines to be detected, and the Doppler shift due to the relative motion of the planet and Earth allows the radiation to penetrate the otherwise absorbing Earth's atmosphere. Latitude masks have been used to measure the latitudinal variation in intensity on Mars, and, by determining intensities over about 30 rotational lines, Boltzmann temperatures were calculated.

The Atmospheric Band system $(O_2(b\,^1\Sigma_g^+ \to X\,^3\Sigma_g^-))$ is strong in the terrestrial dayglow, and is easily observed by rocket photometry. Wallace and Hunten [18] measured the altitude distribution of $O_2(^1\Sigma_g^+)$ using emission of the (0, 0) band at λ = 762 nm for the height range 35 - 238 km, and of the (0, 1) band at λ = 864 nm for the range 59 - 95 km. Emission of the (0, 1) Atmospheric Band is also prominent [19] in the nightglow received at the Earth's surface, and several recent rocket measurements of the (0, 0) Band have been reported [20 - 23]. The Atmospheric Band is not expected to be an important component of Venusian or Martian airglow because of the rapid quenching of $O_2(^1\Sigma_g^+)$ by CO_2 [24, 25].

Of the three singlet states of O_2 that correlate with ground state, ^{3}P, oxygen atoms, the highest is $c\,^1\Sigma_u^-$ whose v' = 0 excitation energy is [26] 4.05 eV. A big impetus to the gas phase study of this species was provided by the observation of $c\,^1\Sigma_u^- \to X\,^3\Sigma_g^-$ emission in the airglows of Venus and Earth. A component of Venusian nightglow [27] was subsequently identified [28] as resulting from a Herzberg II (c $\to$ X) progression in O_2, overlapped [29] by weaker bands of the $A'\,^3\Delta_u \to a\,^1\Delta_g$ system. By computing synthetic spectra for $A\,^3\Sigma_u^+ \to X\,^3\Sigma_g^-$, $A'\,^3\Delta_u \to a\,^1\Delta_g$ and $c\,^1\Sigma_u^- \to X\,^3\Sigma_g^-$ transitions,

Slanger and Huestis [30] were then able to show that the Herzberg II emission had already been recorded [19] in the terrestrial nightglow. However, the intensity of the Herzberg II bands is nearly 30 times weaker on Earth [30, 31] than on Venus, and the vibrational distribution is totally different [30], with emission from $v' = 7$ being dominant in the terrestrial spectrum and $v' = 0$ alone contributing to the Venusian emission. In the Martian airglow, the Herzberg II system is reported [32] as being at least 3 - 4 times weaker than on Earth.

Table 1 summarizes some representative data for the singlet O_2 emissions in the planetary airglows.

TABLE 1

Contributions of singlet O_2 emissions to the airglows of Earth, Venus and Mars

Planet	System	Time or location	Intensity[a]	Approximate height of maximum emission (km)	Reference
Earth	$^1\Delta_g$ - $^3\Sigma_g{}^-$	Day	20 MR	50	[33]
		Night	80 kR	90	[33]
	$^1\Sigma_g{}^+$ - $^3\Sigma_g{}^-$	Day	300 kR	40 - 120	[33]
		Night	6 kR	80 - 90	[33]
	$^1\Sigma_u{}^-$ - $^3\Sigma_g{}^-$	Night	100 R	—	[30]
Venus	$^1\Delta_g$ - $^3\Sigma_g{}^-$	"Day"	4.3 MR[b]	—	[17]
		"Night"	3.4 MR[b]	—	[17]
	$^1\Sigma_u{}^-$ - $^3\Sigma_g{}^-$	"Night"	2.7 kR	—	[31]
Mars	$^1\Delta_g$ - $^3\Sigma_g{}^-$	North pole winter	26 ± 5 MR	—	[16]
		South pole summer	11 ± 2 MR	—	[16]
		Equator	3 ± 1 MR	—	[16]
	$^1\Sigma_u{}^-$ - $^3\Sigma_g{}^-$	—	<30 R	—	[32]

[a] Intensities are given in units of rayleighs (R). 1 rayleigh is the brightness of a source emitting 10^6 photons $cm^{-2} s^{-1}$, in all directions. For an optically thin medium, therefore, the Rayleigh brightness is equivalent to the photon volume emission rate multiplied by the depth of the emitting layer in units of 10 km (10^6 cm). Since 10 km is a typical thickness for an airglow emission "layer", the convenience of the unit is that the Rayleigh brightness is numerically identical with the volume emission rate in photons per cubic centimetre per second.
[b] These intensities may be too high because of a calibration error. Yung and DeMore [34] give the values for day and night as 1.5 MR and 1.2 MR respectively.

3. Excitation mechanisms

Electronic excitation in the neutral atmosphere always derives ultimately from photochemical processes, but there may be one or more steps separating the initial absorption event from the excitation process. Optical absorption in the "chemically active" visible and UV regions usually populates upper

electronic states directly, and the fragments of photodissociation are also themselves frequently excited. At one step further removed from the absorption process, energy-rich species formed in the primary photochemical event may transfer energy directly to acceptor molecules. Processes such as these are confined to periods during, or shortly after, illumination, and are thus important in dayglow excitation. At night, ground state species of high chemical energy may participate in processes in which some of the reaction ergicity appears as electronic excitation of the products. The reactants are frequently (but not always) atoms or radicals, and they are the products of photochemical events that occur during the day. Energy transfer can, of course, lead to population of species chemically distinct from those first excited in the exoergic reaction.

3.1. Primary photochemical processes
Direct absorption of radiation

$$O_2 + h\nu \longrightarrow O_2{}^* \tag{1}$$

can populate singlet O_2 from the ground state in spite of the forbidden nature of the transitions. In the laboratory, both $O_2({}^1\Delta_g)$ and $O_2({}^1\Sigma_g{}^+)$ have been excited, generally using laser sources [24, 35 - 41] but also [42] sometimes with conventional continuous wave broad band lamps. Resonance excitation of singlet O_2 in the atmosphere is significant for $O_2({}^1\Sigma_g{}^+)$:

$$O_2 + h\nu_{\lambda\,=\,762\,nm} \longrightarrow O_2({}^1\Sigma_g{}^+) \tag{2}$$

Between altitudes of 65 and 100 km, reaction (2) is the dominant [18] excitation process for the species in the Earth's dayglow.

Formation of singlet O_2 as a primary photolytic fragment is the most important source of the ${}^1\Delta_g$ state of O_2 by day. Daytime concentrations of $O_2({}^1\Delta_g)$ are so high in the Earth's atmosphere that energy balance considerations alone [43] seem to rule out all sources other than photolysis of O_3 in the UV region:

$$O_3 + h\nu_{UV} \longrightarrow O_2({}^1\Delta_g) + O({}^1D,\,{}^3P) \tag{3}$$

Several laboratory studies [44 - 49] have established that $O_2({}^1\Delta_g)$ is formed in the process; rotational state distributions may be anomalous, with even-J states favoured [50]. The absolute quantum yield for $O_2({}^1\Delta_g)$ production was measured [49] as 0.83 ± 0.11 at $\lambda = 253.7$ nm. The conventional interpretation of O_3 photolysis in the UV has been that singlet spin multiplicity is conserved throughout the absorption and fragmentation process, so that the possible atomic and molecular fragments are either two triplets ($O_2({}^3\Sigma_g{}^-)$ + $O({}^3P)$) or two singlets: the lowest singlet pair is $O_2({}^1\Delta_g)$ + $O({}^1D)$ for which the threshold wavelength is about 310 nm. Various studies [51 - 57] show that the quantum yield for $O({}^1D)$ formation falls for $\lambda > 300$ nm. The exact form of the fall-off curve is temperature dependent [58 - 60], and $O({}^1D)$ quantum yields are particularly temperature sensitive at 300 nm $< \lambda <$ 310 nm.

Vibrational (and rotational) excitation in O_3 probably contributes to the total dissociation energy in the critical region [46, 61]. Other singlet molecular (*e.g.* $O_2(^1\Sigma_g^+)$ [48]) or atomic (*e.g.* $O(^1S)$ [62]) fragments possible at shorter wavelengths are, in reality, formed with very low yields.

Two experimental facts slightly modify the neat picture of thermodynamically controlled spin-conserved photodissociation of O_3. The first concerns the absolute yields of $O(^1D)$ formed at wavelengths less than the threshold (about 310 nm). Evidence is accumulating [63 - 67] that about 10% of the photolysis goes via a channel yielding $O(^3P)$. Time-of-flight photofragmentation experiments (*e.g.* those of Sparks *et al.* [66]) provide a particularly clear demonstration both that $O_2(^1\Delta_g) + O(^1D)$ is the major product pair and that $O_2(^3\Sigma_g^-) + O(^3P)$ is nevertheless a significant minor channel at $\lambda = 266$ nm. The results thus suggest that the absolute quantum yield for $O_2(^1\Delta_g)$ production should also be less than unity, and that the measured [49] yield of 0.83 ± 0.11 should *not* be interpreted as meaning unity! A second modification to the simple interpretation of O_3 photolysis concerns the quantum yield for $O_2(^1\Delta_g)$ production at wavelengths *longer* than the $\lambda \approx 310$ nm threshold. Laboratory experiments [51, 52, 68] show that $O_2(^1\Delta_g)$ is formed unexpectedly with nearly 100% efficiency at $\lambda = 334$ nm. However, if $O_2(^1\Delta_g)$ is produced, it can be accompanied only by $O(^3P)$ at the photon energy available, so that the photodissociation is spin disallowed. Either a triplet state of O_3 is populated by a direct, but forbidden, optical transition at $\lambda = 334$ nm, or optical absorption in the singlet system may be followed by forbidden crossing to the triplet at this wavelength. A state of O_3 that could possibly be identified with this triplet is the $2\,^3B_2$, on the basis of a comparison of observed [69] and computed [70, 71] excited states of O_3.

Data on quantum yields for singlet O_2 production in reaction (3) and on quenching rate coefficients may be combined with experimentally determined atmospheric O_3 concentrations and solar irradiances to predict the $[O_2(^1\Delta_g)]$–altitude profile. Figure 3 shows the results of one such calculation [72] together with some data from rocket measurements [73, 74] for the Earth's dayglow. The good agreement may be taken as confirming the O_3 photolysis mechanism for $O_2(^1\Delta_g)$ production, and further confidence is lent by the close similarity of quenching rates determined from eclipse observations [7] and in the laboratory [75 - 77]. Indeed, confidence in the model is now so great that it is frequently inverted, and measurements of the IR Atmospheric Band intensities in the dayglow are used to deduce atmospheric O_3 concentrations and profiles. For example, a secondary peak found [11] in dayglow emission intensity at about 90 km is taken [7] to be associated with a secondary maximum in $[O_3]$ at this altitude. Instruments on the Solar Mesosphere Explorer satellite now routinely obtain [78] atmospheric O_3 concentration distributions from the intensity of emission at $\lambda = 1.27\ \mu m$.

As on Earth, O_3 photolysis appears to be the only reasonable source of the amounts of $O_2(^1\Delta_g)$ present in the Martian atmosphere [15, 16]. Catalytic
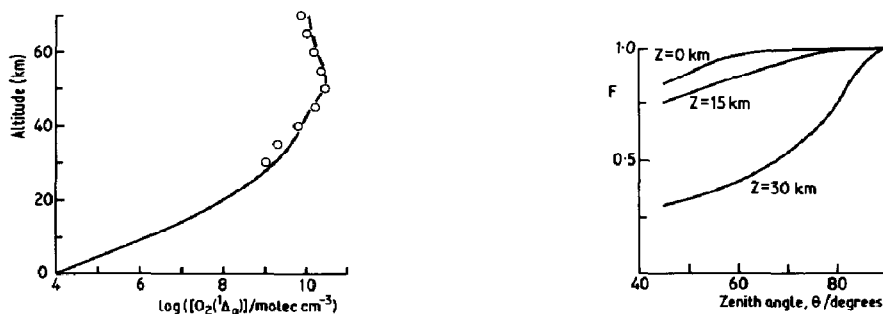
Fig. 3. Calculated and experimental concentration–altitude profiles for $O_2(^1\Delta_g)$ in the Earth's daytime atmosphere during spring: ———, calculations from ref. 72; o, experimental values based on refs. 73 and 74.

Fig. 4. The effect of $O_2(^1\Delta_g)$ formation in O_3 photolysis at $\lambda > 310$ nm. F is the fraction of $O_2(^1\Delta_g)$ produced beyond the $\lambda = 310$ nm threshold, and is shown as a function of solar zenith angle θ for three different altitudes (northern hemisphere spring) [72].

reactions involving HO_x species play a major role [79] in O_3 loss at low latitudes, but less at high latitudes during winter. Hence O_3 concentrations at the winter pole will be higher, and, with reasonable assumptions [16], the latitudinal variations (Table 1) of the IR Atmospheric Band can be matched. O_3 photolysis cannot be the source of $O_2(^1\Delta_g)$ on Venus because of the low O_2 column densities [80]. The column emission rate [17] (Table 1) on the day side is close to the rate at which oxygen atoms (precursors of O_2 and O_3) are produced by CO_2 photolysis. Only 130 kR of the emission can come from O_3 photolysis [81], an estimate that could, perhaps, be increased by 60% if scattering of solar radiation by SO_2 were included. Alternative excitation mechanisms are considered in Sections 3.3 and 3.4.

It remains, in this section, to consider the influence on dayglow intensities of a quantum yield lower than unity for $O_2(^1\Delta_g)$ formation in O_3 photolysis at $\lambda < 310$ nm, and the non-zero yield at longer wavelengths (probably the yield is the same, about 0.9, as at $\lambda < 310$ nm). The effect of a 10% lower yield of $O_2(^1\Delta_g)$ in the "spin-allowed" dissociation means that predicted dayglow intensities should be 10% lower for a given O_3 concentration and solar irradiance. Conversely, then, O_3 concentrations derived from IR Atmospheric Band measurements may be underestimates by the same relative amount. This factor does not seem to have been explicitly accommodated in the currently available calculations. At altitudes in the atmosphere above about 45 km, most of the dissociation of O_3 is brought about by light of $\lambda < 310$ nm, and the consequences [72] of $O_2(^1\Delta_g)$ production at longer wavelengths are minimal. However, at lower altitudes, or for very low solar elevations (large zenith angles θ), much of the shorter wavelength solar radiation is attenuated. Long wavelength photolysis of O_3 may then contribute substantially to the yield of $O_2(^1\Delta_g)$, and large fractions F of singlet O_2 can be produced in the spin-forbidden region, as shown by model calculations [72] presented in Fig. 4. Near the Earth's surface, almost all $O_2(^1\Delta_g)$ comes

from photolysis at $\lambda > 310$ nm, and, even at about 30 km, more than half comes from this source at solar zenith angles greater than $70°$.

3.2. Energy transfer from primary products

The prime example in singlet O_2 airglow studies of transfer excitation from the energy-rich products of primary photolysis is the formation of $O_2(^1\Sigma_g^+)$ in the process

$$O(^1D) + O_2(^3\Sigma_g^-) \longrightarrow O_2(^1\Sigma_g^+) + O(^3P) \qquad (4)$$
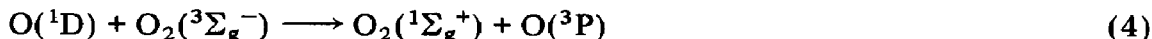
In the Earth's atmosphere, the process supplements resonance scattering (reaction (2)) at all altitudes, and dominates [18] above 100 km and below 65 km. Excited, ^1D, oxygen atoms come from O_3 photolysis, reaction (3), in the lower altitude region, and from O_2 photolysis

$$O_2 + h\nu \longrightarrow O(^1D) + O(^3P) \qquad (5)$$

in the higher one.

Wallace and Hunten [18], in assessing atmospheric excitation rates, assumed that all quenching of $O(^1D)$ by $O_2(^3\Sigma_g^-)$ leads to excitation of $O_2(^1\Sigma_g^+)$. After some false starts, laboratory measurements also [82 - 84] now indicate at least a "high" (greater than 60%) transfer efficiency. The most direct determination appears to be that of Lee and Slanger [84], who used laser flash photolysis of O_2 as a source of $O(^1D)$, and followed both $[O(^1D)]$ and $[O_2(^1\Sigma_g^+, v' = 0, 1)]$. The results show that $77\% \pm 20\%$ of quenching collisions are accompanied by $O_2(^1\Sigma_g^+)$ formation. Donovan and Husain [85] have explained in terms of correlation diagrams why most of the $O(^1D)$ quenching should yield $O_2(^1\Sigma_g^+)$. The system $O(^1D) + O_2(^3\Sigma_g^-)$ lies at an energy only about 1750 cm^{-1} above that of $O(^3P) + O_2(^1\Sigma_g^+)$. Close proximity of the potential energy surfaces should enhance the probability of transitions of the type $A' \leftrightarrow A''$ with no change of spin, since the complex will persist for 10^{-11} - 10^{-12} s.

3.3. Atom recombination

Two ground state oxygen atoms correlate with the three singlet excited states of O_2 (see Fig. 1), so that recombination might well excite O_2^*:

$$O + O + M \longrightarrow O_2^* + M \qquad (6)$$

The overall rate constant is known, and Campbell and Gray [86] have measured the temperature dependence of the reaction rate. Since oxygen atoms decay relatively slowly at night in the Earth's atmosphere, and have almost the same concentration on day and night sides of Venus [87], the reactions summarized by process (6) seem at first sight to be attractive candidates for excitation of the Atmospheric and IR Atmospheric Bands in the nightglow from the planets.

Excited states of O_2 are certainly produced in the recombination of oxygen atoms in the laboratory, but for the $a\,^1\Delta_g$ and $b\,^1\Sigma_g^+$ states the experimental data are rather sparse. Various surprising and important findings have

emphasized the need for care in interpreting the data. For example, Black and Slanger [88] have shown that up to 25% of loss of oxygen atoms on a Pyrex wall can yield $O_2(^1\Delta_g)$. At this conference, evidence is presented [89] to show that $O_2(b\,^1\Sigma_g^+)$ formation in reaction (6) is even less efficient than hitherto supposed. Curiously, rather more information seems to be available about formation of the generally less studied singlet, $c\,^1\Sigma_u^-$, in reaction (6). Lawrence *et al.* [28] were able to obtain a progression of bands from $v' = 0$ of $O_2(c\,^1\Sigma_u^-)$ by adding CO_2 (about 10 Torr) downstream of a discharge in a flow system carrying 0.3% O_2 in helium at 22 Torr. At first, it seemed as though CO_2 was essential in producing $O_2(c\,^1\Sigma_u^-)$, and that a specific excitation process

$$O + O + CO_2 \longrightarrow O_2(c\,^1\Sigma_u^-) + CO_2 \tag{7}$$

was implicated. However, it has become clear [26, 90, 91] that CO_2 is not a necessary ingredient, although emission of the Herzberg II bands is undoubtedly stronger when it is present. Emission is even observed [26, 90] when O is generated in the absence of O_2, so that $O_2(c\,^1\Sigma_u^-)$ is formed strictly by oxygen atom recombination. The peculiar influence of CO_2 is then seen either in its efficiency as a third body in recombination or in its influence in promoting vibrational–vibrational relaxation and cross relaxation to funnel most of the excited population of A, A' and c states to $O_2(c\,^1\Sigma_u^-$, $v' = 0)$. A number of other third bodies [91] (*e.g.* CCl_4 and some chlorofluorocarbons) whose vibrational spacings match those in the A, A' and c states are almost as effective as CO_2 in populating $O_2(c\,^1\Sigma_u^-)$. It is clear from the experiments that neither N_2 nor CO_2 is a strong quencher of the $c\,^1\Sigma_u^-$ state, but that CO_2 strongly quenches the A and A' states of O_2.

Theoretical calculations have been presented of the passage into the various possible channels of the products of reaction (6). It is evident that the relative populations in the different molecular states are not determined simply by the statistical weighting of the orbital and spin degeneracies. Other factors, such as rotational barriers, must operate at large atomic internuclear separation to favour particular molecular electronic states. Wraight [92] determines the probability of stabilizing collisions with M, integrated over classical motions of interacting oxygen atoms, using the potential energy curves of Saxon and Liu [93]. Figure 5 shows the results of the calculations. At face value, the figure suggests rather small fractions of direct association into $^1\Delta_g$ or $^1\Sigma_g^+$ states. Most of the recombination (more than 70% at low temperatures) goes through a state identified as $^5\Pi_g$ whose weak binding energy (a few tenths of an electronvolt) accounts for the large negative temperature coefficient found experimentally for the total recombination process.

Demands placed by airglow intensity measurements on excitation efficiency may now be considered in the light of the experimental evidence reviewed above. Llewellyn and Solheim [94] suggest a tendency for night-time $[O_2(^1\Delta_g)]$ and [O] to co-vary when [O] is high, and they interpret this result to mean that the reaction
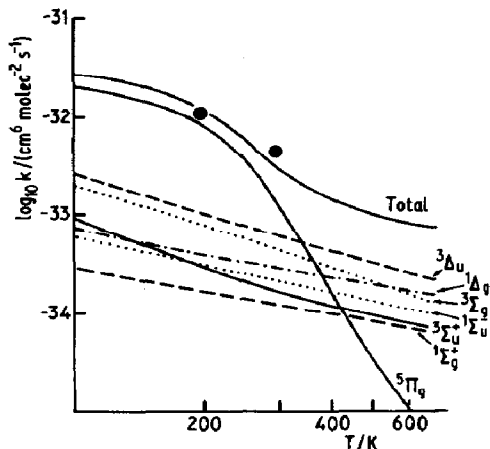
Fig. 5. Calculated rate coefficients for association of oxygen atoms via different electronic states of O_2 [92]: ●, experimental points taken from Campbell and Gray [86].

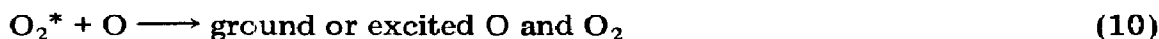$$O + O + M \longrightarrow O_2({}^1\Delta_g) + M \tag{8}$$

is the dominant night-time source of $O_2({}^1\Delta_g)$ in the Earth's atmosphere at high [O]. However, 25% of oxygen atom recombination would have to yield $O_2({}^1\Delta_g)$ if the measured intensities are to be matched. Such a high fraction does not seem generally consistent with laboratory measurements, although Yung and DeMore [34] do quote an unpublished estimate of Ogryzlo that puts the efficiency of $O_2({}^1\Delta_g)$ formation as high as 30%, comparable with the heterogeneous production efficiency [88]. According to the most probable [34] model of Venusian stratospheric chemistry, reaction (8) could then account for about 650 kR, or about one-half, of the observed (and corrected) emission intensity. Witt et al. [22] are persuaded that the reaction analogous to (8)

$$O + O + M \longrightarrow O_2({}^1\Sigma_g{}^+) + M \tag{9}$$

cannot be the source of $O_2({}^1\Sigma_g{}^+)$ in the terrestrial nightglow, on the basis of their rocket measurements. The Atmospheric Band intensity requires that the efficiency of $O_2({}^1\Sigma_g{}^+)$ formation be more than statistically favoured. Peak emission altitudes can be matched only if a rate constant is adopted for the quenching of $O_2({}^1\Sigma_g{}^+)$ by O that is at least 50 times greater than the measured value [95, 96]. The weight of evidence thus argues against atomic recombination being a significant direct source of the $b\,{}^1\Sigma_g{}^+$ state in the planetary atmospheres. The situation with regard to ${}^1\Delta_g$ remains open to doubt, and further experimental evidence is eagerly awaited.

In contrast with the situation for ${}^1\Delta_g$ and ${}^1\Sigma_g{}^+$ states, direct recombinative excitation does seem to be a possible source of the $O_2(c\,{}^1\Sigma_u{}^-)$ found in the atmospheres of Earth, Venus and possibly Mars. Before the laboratory experiments [26, 90] had been performed, Krasnopolski et al. [27] had already questioned the specific role of CO_2 in promoting formation of $O_2(c\,{}^1\Sigma_u{}^-)$. Emission of the Herzberg II system from Mars is very weak
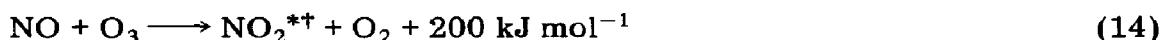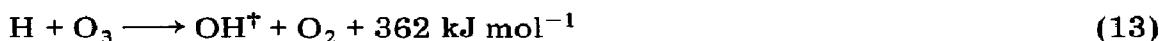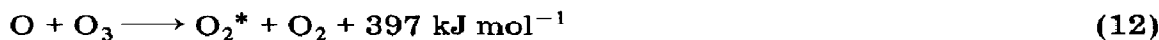
(Table 1), yet the atmosphere, like that of Venus, is composed predominantly of CO_2. O_2 is at least 1000 times as abundant on Mars as on Venus, in terms of mixing ratios, so that quenching of $O_2(^1\Sigma_u^-)$ might suppress the Herzberg II bands on Mars [27]. Kenner *et al.* [91] have tested the hypothesis, but their kinetic evidence shows that it is O, rather than O_2, that quenches $O_2(^1\Sigma_u^-)$ most strongly. Some modifications have been made [97] to the original [91] kinetic scheme that purport to be consistent with the relative intensities of Herzberg I and II bands in the airglows of Earth, Mars and Venus. The most important elements [97] of the modified scheme are the quenching of O_2^* formed as the initial product of atom recombination in reaction (6) with O_2 and O to give quenched products that may themselves include new excited states of O_2 and O, as represented by the general equations

$$O + O + M \longrightarrow O_2^* + M \tag{6}$$

$$O_2^* + O \longrightarrow \text{ground or excited O and } O_2 \tag{10}$$

$$O_2^* + O_2 \longrightarrow \text{ground or excited } O_2 \tag{11}$$

The state O_2^* is *not necessarily* to be identified with $O_2(c\,^1\Sigma_u^-)$. Reactions (10) and (11) are both formally energy transfer processes, and further discussion of them will be deferred until Section 3.5.

3.4. Metathetical chemical reaction

We may conveniently start by dismissing some reactions that have been suggested as sources of singlet O_2, but which laboratory experiments have failed to substantiate. The three reactions
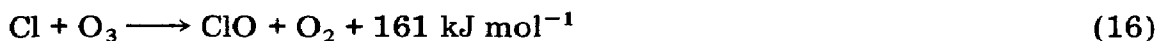
$$O + O_3 \longrightarrow O_2^* + O_2 + 397 \text{ kJ mol}^{-1} \tag{12}$$

$$H + O_3 \longrightarrow OH^\dagger + O_2 + 362 \text{ kJ mol}^{-1} \tag{13}$$

$$NO + O_3 \longrightarrow NO_2^{*\dagger} + O_2 + 200 \text{ kJ mol}^{-1} \tag{14}$$

are all sufficiently exothermic to populate $^1\Delta_g$ or $^1\Sigma_g^+$ states of O_2 (excitation energies of 94.3 kJ mol^{-1} and 157 kJ mol^{-1} respectively), and the first reaction could even excite the $^1\Sigma_u^-$ state (390 kJ mol^{-1}). Although reactions (12) and (13) yield high degrees of vibrational excitation in the newly formed O—O or O—H bond, and vibronically excited NO_2 is formed in reaction (14), no evidence has ever shown that the O_2 product is electronically excited. Washida *et al.* [98], using photo-ionization mass spectrometry presumably sensitive to all three singlet states, find that the fraction of reaction leading to excited O_2 is less than 0.06, less than 0.002 and less than 0.001 for reactions (12), (13) and (14) respectively. Limiting fractions of less than 0.003 and less than 0.005 have been determined [99] for the formation of the individual states $^1\Delta_g$ and $^1\Sigma_g^+$ in reaction (14), and molecular beam studies [100] also fail to detect any reaction channel leading to singlet O_2. The preference for excited NO_2 rather than O_2 suggests [101] that there must be a strong energetic requirement for symmetry to be preserved in the interaction, as otherwise $O_2(^1\Delta_g)$ could be formed from the $J = 3/2$ level of NO.

Since $OH^{\dagger}$ with $v'' \leqslant 9$ is formed in reaction (13) and is known to be present in the upper atmosphere at night, it seems possible that the species is a precursor of singlet O_2 in the Earth's nightglow. Reaction between O and OH

$$O + OH(v'') \longrightarrow O_2 + H \tag{15}$$

is only about 70 kJ mol^{-1} exothermic for unexcited OH and O_2, so that v'' in $OH^{\dagger}$ must be at least 1 (equivalent to 42.7 kJ mol^{-1} of vibrational energy) for $O_2(^1\Delta_g)$ production, and probably 4 (equivalent to 159.1 kJ mol^{-1}) for $O_2(^1\Sigma_g^+)$. For $v'' = 0$, 84% ± 7% of the ergicity of reaction (15) goes into product translational energy [102].

As pointed out in Section 3.1, the low O_2, and hence O_3, concentrations in the Venusian atmosphere make O_3 photolysis at most a minor contributor to the Venusian IR Atmospheric Band emission. Yung and DeMore [34] find the probable daytime emission intensity to be about 130 kR, which is seen [34] to be consistent with the night–day intensity difference. Even the disputed high (about 30%) population of $O_2(^1\Delta_g)$ by oxygen atom recombination (Section 3.3) seems to be unable to account for all the remaining Venusian $O_2(^1\Delta_g)$, and other sources of singlet O_2, however esoteric, must be sought. Reactions of Cl_x species have been proposed, with the favoured processes [17, 34, 80, 87] being

$$Cl + O_3 \longrightarrow ClO + O_2 + 161 \text{ kJ mol}^{-1} \tag{16}$$

$$ClO + O \longrightarrow Cl + O_2 + 236 \text{ kJ mol}^{-1} \tag{17}$$

Each reaction is sufficiently exothermic to populate either $O_2(^1\Delta_g)$ or $O_2(^1\Sigma_g^+)$. Together the processes represent a catalytic chain, but the chain needs to be fed by O_3 as well as by O. We recall that the emission rate on Venus is close to the rate at which oxygen atoms are liberated by photodissociation of CO_2, so that reaction (17) seems to be the more likely Venusian source, and it has also the virtue that the electronic excitation is required to be present in the newly formed O—O bond rather than in the moiety left over as in reaction (16). However, reaction (17) could proceed (on a quartet surface) to triplet O_2, while reaction (16) can only yield singlet O_2 in a spin-conserved interaction proceeding via a doublet surface. Watson, in his review of Cl_x reactions [103], actually explicitly writes the O_2 product of reaction (17) as in one or other of the singlet states, but apparently without evidence. Oxygen *atoms* have been seen [104] as a secondary product of the reaction between Cl and O_3, and their appearance ascribed to O_2^* formation in reaction (16) followed by oxygen atom generation in the decomposition of O_3 by the O_2^*. Kinetic evidence favours the $^1\Sigma_g^+$ state for O_2^*, with an excitation efficiency of less than 1% [104]. Thus $O_2(^1\Delta_g)$ production in either reaction needs experimental test. A further speculation concerns the abundance of chlorine-containing compounds in the atmosphere of Venus. Recent investigations of Venusian atmospheric composition are reviewed by Moroz [105]. Ground-based spectrometry indicates a stratospheric mixing ratio for HCl of about $(4 - 6) \times 10^{-7}$; Cl_2 may be present at

70 km at a mixing ratio of about 10^{-6}. Optical spectrometry from Venera 11, 12 gives a Cl_2 mixing ratio of 10^{-7} in the 0 - 60 km region, and X-ray fluorescence studies on Venera 12 show that the most abundant component in the cloud particles is chlorine containing. Pioneer–Venus studies show little evidence of chlorine compounds! However, it is generally held that free Cl_x radicals play a major role in cyclic catalysed oxidation of CO to CO_2, and hence in maintaining the photochemical stability of CO_2. Current models of the Venusian stratosphere [34] certainly show that the CO_2 stability can be adequately explained in terms of a catalytic mechanism propagated by Cl, ClCO and $ClCO_3$ amongst other species. Yung and DeMore [34] show that, in the most likely of their models, reactions (16) and (17) could contribute about 150 kR and 290 kR respectively to the Venusian airglow. A further 50 kR could come from yet another hypothetical excitation process, this time involving HO_x species:

$$O + HO_2 \longrightarrow OH + O_2 + 220 \text{ kJ mol}^{-1} \tag{18}$$
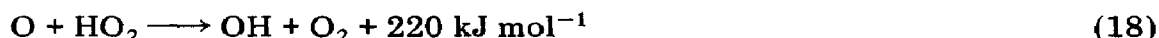
which had already been postulated [14] as a contributor to singlet O_2 excitation in the Earth's nightglow.

We have seen, in this section, that there is no shortage of speculation or inventiveness about mechanisms by which singlet O_2 *might* become excited. Rather, it is the experimental validation of such mechanisms that remains questionable. Three of the proposed reactions (reactions (12) - (14)) seem to be excluded by the laboratory evidence. However, four others (reactions (15) - (18)) are in need of detailed investigation.

3.5. Secondary energy transfer

As we have seen in the preceding two sections, there remains considerable doubt about whether oxygen atom recombination or chemical reaction can produce directly as much $O_2(^1\Delta_g)$ or $O_2(^1\Sigma_g^+)$ as is seen in the Earth's nightglow, or as much $O_2(^1\Delta_g)$ as is present in the Venusian stratosphere. In view of these difficulties, it is natural to look for alternative, *indirect*, sources of excitation, in which O_2 receives its energy by transfer from a donor generated from precursors that persist by night. One possibility that has received consideration for some time is that vibrationally excited $OH^\dagger$, formed in reaction (13), might produce electronically excited O_2 in a collisional exchange process:

$$OH^\dagger(v'') + O_2 \longrightarrow O_2^* + OH \tag{19}$$

An additional 70 kJ mol^{-1} of energy must be found for excitation of the O_2^* states compared with that needed in the exchange reaction (15) with oxygen atoms. Nevertheless, reaction (13) is, in principle, exothermic enough to provide sufficient energy in $OH^\dagger$ to excite either $O_2(^1\Delta_g)$ or $O_2(^1\Sigma_g^+)$. Several investigators have looked for co-variations in atmospheric $[O_2^*]$ and $[OH^\dagger]$. Thus, Llewellyn and Solheim [94] see a dependence on the $OH^\dagger$ emission intensity of $[O_2(^1\Delta_g)]$ under conditions of high $[OH^\dagger]$, and similar correlations have been sought [23] between $[OH^\dagger]$ and $[O_2(^1\Sigma_g^+)]$. However,

it is difficult to match derived concentration–altitude profiles [22, 23] without recourse to implausible rate coefficients, and Witt *et al.* [22] believe that reaction (19) cannot be the source of $O_2(^1\Sigma_g^+)$ on the basis of their rocket measurements, which provide a simultaneous direct measure of $[O_2(^1\Sigma_g^+)]$ and [OH] and an indirect measurement of [O]. In any case, rate coefficients for quenching by O_2 of vibrational excitation in OH are relatively small for $4 < v'' < 9$ (*e.g.* about 1.4×10^{-13} cm^3 molecule^{-1} s^{-1} for $v'' = 4$), so that production of singlet O_2 in reaction (19) must also be slow. This limitation on rate makes the process unlikely to be a major contributor to the terrestrial airglow.

Energy transfer of a rather different kind has been increasingly suggested in recent years to account for atmospheric excitation of $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g^+)$. Given that the atomic recombination reaction

$$O + O + M \longrightarrow O_2^* + M \tag{6}$$

is very inefficient at populating $O_2(^1\Sigma_g^+)$ directly, and that its efficiency in populating $O_2(^1\Delta_g)$ is strongly disputed (Section 3.3), considerable speculation [95] has arisen to suggest that the higher state O_2^* first formed can undergo energy transfer (or quenching) collisions with O_2 or O to populate the lower states $^1\Sigma_g^+$ or $^1\Delta_g$. Formally, then, the reactions envisaged are processes (10) and (11), which may now be written out as

$$O_2^* + O_2 \longrightarrow O_2(^1\Sigma_g^+) + O_2 \tag{20}$$

$$O_2^* + O \longrightarrow O_2(^1\Delta_g) + O \tag{21}$$

The scheme has the virtue in airglow interpretations that the Atmospheric Band intensity now depends on $[O_2][M]$ as well as $[O]^2$, and it becomes easy to reconcile the observed altitude of peak intensity with sensible rate parameters [95]. An upper peak in the IR Atmospheric Band intensity–altitude profile is predicted to follow [O], as observed [13].

Ideas about two-step excitation of $O_2(^1\Delta_g)$ or $O_2(^1\Sigma_g^+)$ in reactions (6) and (20) or (21) are developing in parallel with an increasing awareness that excited O_2 is a possible precursor of $O(^1S)$, the state responsible for the strongest atomic emission ($\lambda = 557.7$ nm) in the Earth's airglow. For years, controversy existed over the relative merits of the one-step [106] "Chapman"

$$O + O + O \longrightarrow O(^1S) + O_2 \tag{22}$$

and the two-step [107, 108] "Barth"

$$O + O + M \longrightarrow O_2^* + M \tag{6}$$

$$O_2^* + O \longrightarrow O(^1S) + O_2 \tag{23}$$

excitation mechanisms. Apparent anomalies in the laboratory data have now been resolved [109 - 111] and theoretical and experimental considerations [14, 32, 95, 97, 112 - 117] almost all now favour the "Barth" mechanism. For the present purposes, the interest lies in the similarity of reactions (21) and (23). In the first, attention is focused on excitation in the molecular

product and in the second on the atomic one. However, both involve an excited molecular reactant formed by the recombination of oxygen atoms.
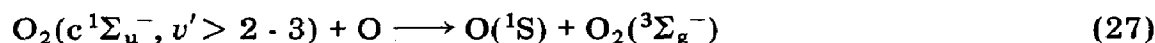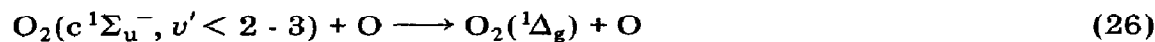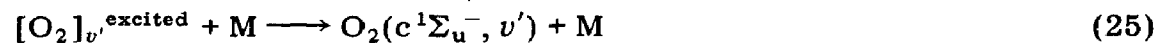
It remains for us to speculate about the possible identities of O_2^* in reactions (6), (20), (21) and (23), and whether it might even be the same state, at least electronically, in the three energy transfer steps. These speculations form the substance of several later presentations in this conference session, and are introduced in the next section.

4. Is O_2^* to be identified with $O_2(c\,^1\Sigma_u^-)$?

Not surprisingly, the discovery that the relatively high-lying singlet, $c\,^1\Sigma_u^-$, is indeed populated by atom recombination has made this state a prime target for the speculations. Greer *et al.* [95] explicitly suggest that $O_2(^1\Sigma_u^-)$ is the intermediate in reactions (20) and (21), and point out that it can populate $v' = 5$ in $O_2(^1\Sigma_g^+)$ from its ground vibrational level. At atmospheric altitudes of about 100 km, vibrational relaxation will be rapid, but at higher altitudes such an excitation mechanism could explain the vibrational development seen in aurorae by Gattinger and Vallance-Jones [118]. Conversely, Ogryzlo *et al.* [89] show that, although a reaction such as reaction (20) indeed seems to populate $O_2(^1\Sigma_g^+)$ in laboratory experiments, the results indicate that O_2^* cannot be identified with the lower vibrational levels of $O_2(c\,^1\Sigma_u^-)$ (or for that matter of the $A\,^3\Sigma_u^+$ or $A'\,^3\Delta_u$ states). Wraight [92] favours the weakly bound $^5\Pi_g$ state as the intermediate, since his calculations show it to be responsible for more than 70% of recombination at low temperatures (*cf.* Section 3.3 and Fig. 5).

Potential candidates for O_2^* in reaction (23) that yields $O(^1S)$ include the $c\,^1\Sigma_u$, $A'\,^3\Delta_u$ or $A\,^3\Sigma_u^+$ states. The $O(^1S)$ excitation energy is 4.19 eV, and the $v' = 0$ levels of c, A' and A states lie at 4.05 eV, 4.24 eV and 4.34 eV respectively. Bates [116] reviews evidence from terrestrial airglow experiments that makes the $A\,^3\Sigma_u^+$ state a rather unattractive candidate as the $O(^1S)$ precursor, the relatively intense emission from A as compared with A' or c states reflecting transition probabilities [26] rather than atmospheric abundances. Venusian nightglow measurements [32] point in the direction of the c state. Green line emission is very weak, so that the precursor is absent in the Venusian upper atmosphere but present in Earth's. The $v' = 0$ levels of c, A' and A states are all present [31] on Venus, but the c state lies just *below* $O(^1S)$ while the others lie above. An activation energy for reaction (23) of the order of the energy deficit of 0.14 eV would make the process slow, and the emission weak, since $T \approx 188$ K at those altitudes in the Venusian atmosphere where [O] is highest. Vibrational relaxation in $O_2(c\,^1\Sigma_u^-)$ in the Earth's atmosphere is much less pronounced than on Venus (Section 2), and the peak intensity of the Herzberg II bands comes from $v' = 7$. Vibrational excitation could overcome the activation barrier for reaction (23), which becomes exothermic for v' greater than 2 or 3 in $O_2(c\,^1\Sigma_u^-)$.
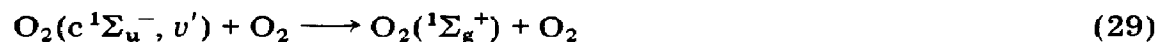
If, then, $O_2(c\,^1\Sigma_u^-)$ is, in reality, O_2^* not only in reaction (23) but also in reaction (21), a single mechanism may be drawn up for excitation of $O(^1S)$ and $O_2(^1\Delta_g)$ in the Earth's nightglow:

$$O + O \rightleftharpoons [O_2]_{v'}^{\text{excited}} \tag{24}$$

$$[O_2]_{v'}^{\text{excited}} + M \longrightarrow O_2(c\,^1\Sigma_u^-, v') + M \tag{25}$$

$$O_2(c\,^1\Sigma_u^-, v' < 2 \cdot 3) + O \longrightarrow O_2(^1\Delta_g) + O \tag{26}$$

$$O_2(c\,^1\Sigma_u^-, v' > 2 \cdot 3) + O \longrightarrow O(^1S) + O_2(^3\Sigma_g^-) \tag{27}$$

The weakly bound intermediate, $[O_2]_{v'}^{\text{excited}}$, may well be the $^5\Pi_g$ favoured by Wraight [92], and collisional deactivation can then yield $O_2(A^3\Sigma_u^+, A'^3\Delta_u)$ as well as the singlet $c\,^1\Sigma_u^-$ state. Increased vibrational relaxation at lower altitudes predicts a peak in $[O_2(^1\Delta_g)]$ below the peak in either $[O(^1S)]$ or $[O(^3P)]$, in agreement with the observations [14]. Perhaps the findings of Ogryzlo *et al.* [89] about $O_2(^1\Sigma_g^+)$ formation indicate a specific transfer quenching of the intermediate by O_2

$$[O_2]_{v'}^{\text{excited}} + O_2 \longrightarrow O_2(^1\Sigma_g^+) + O_2 \tag{28}$$
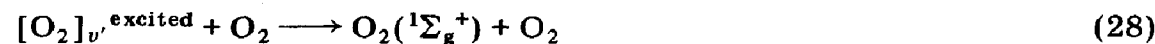
rather than the transfer from $O_2(^1\Sigma_u^-)$

$$O_2(c\,^1\Sigma_u^-, v') + O_2 \longrightarrow O_2(^1\Sigma_g^+) + O_2 \tag{29}$$

envisaged by Witt and coworkers [95, 119]. In either case, the position of the $[O_2(^1\Sigma_g^+)]$ nightglow maximum [95] is determined by competition between high [O] and high $[O_2]$.

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