Rocket Photometry and the Lower-Thermospheric Oxygen Nightglow [and Discussion]

R. G. H. Greer, D. P. Murtagh, I. C. McDade, E. J. Llewellyn, G. Witt, B. A. Thrush, I. P. Stott and S. A. Bowhill

Phil. Trans. R. Soc. Lond. A 1987 **323**, 579-595
doi: 10.1098/rsta.1987.0107

Phil. Trans. R. Soc. Lond. A **323**, 579–595 (1987)
Printed in Great Britain

Rocket photometry and the lower-thermospheric oxygen nightglow

By R. G. H. Greer[1], D. P. Murtagh[2], I. C. McDade[3], E. J. Llewellyn[3] and G. Witt[2]

[1] *Department of Pure and Applied Physics, The Queen's University of Belfast,*
Belfast BT7 1NN, Northern Ireland
[2] *Meteorological Institute, Arrhenius Laboratory, The University of Stockholm, S-106 Stockholm, Sweden*
[3] *Institute of Space and Atmospheric Studies, The University of Saskatchewan,*
Saskatoon, Canada S7N 0N0

Experimental aspects of rocket photometry are briefly discussed in the light of the requirement to measure the nightglow with high accuracy. In relation to measurements of the nightglow Green Line and the (0, 0) Atmospheric Band system, the development of our understanding of their excitation mechanisms in particular and the associated photochemistry in general is traced from Chapman to the present.

1. Introduction

Rocket photometry of airglow phenomena began in 1955 with an experiment by Berg *et al.* (1956) to study the night-time O(^{1}S) Green Line emission at 557.7 nm. To date, some fifty rocket flights carrying airglow payloads have been reported from non-Soviet countries. Although the daytime airglow has occasionally been investigated, for obvious practical reasons most experiments have been conducted at night. All the principal spectral features (Krassovsky *et al.* 1962; Broadfoot & Kendall 1968) in the range roughly 200–2000 nm have now been investigated. Most frequently studied have been those emissions associated with atomic and molecular oxygen and that originate in the lower thermosphere. The variety of these emissions may be better appreciated from the oxygen term diagrams and potential energy curves shown in figure 1.

This paper describes some of the more significant results, both experimental and theoretical, that derive from rocket photometer measurements of the oxygen-related nightglow. Included in these are measurements recently made at The Queen's University of Belfast, where rocket photometry of the nightglow has long been an active research interest. Attention is focused on the Green Line and the Atmospheric Band at 761.9 nm, which feature prominently not only in the nightglow spectrum but also in the development of our understanding of the oxygen photochemistry in the lower thermosphere.

The basic measurement objective is to monitor accurately the variation with altitude of the volume emission rate of selected airglow features. Advances in optical and electronic technology have greatly contributed to the precision with which we can now record such data from space vehicles. However, four aspects of rocket photometry that impinge directly on the integrity of the nightglow data are noteworthy. These are the absolute calibration of the photometers; the determination of the attitude of the photometers' viewing axis during the observing period; the consideration of, and allowance for, possible luminous contamination of the photometer signals by local vehicle-induced luminance in the atmosphere; and, fourthly, the procedure for differentiating the measured integrated data to obtain an emission profile.

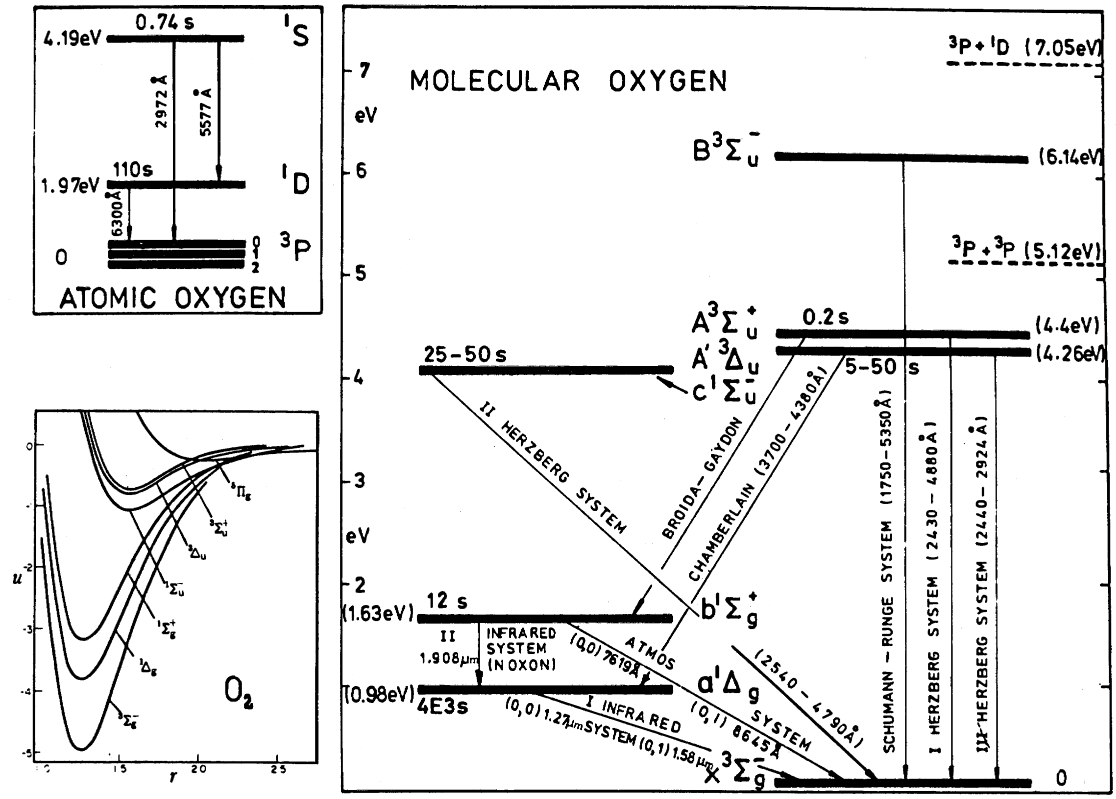
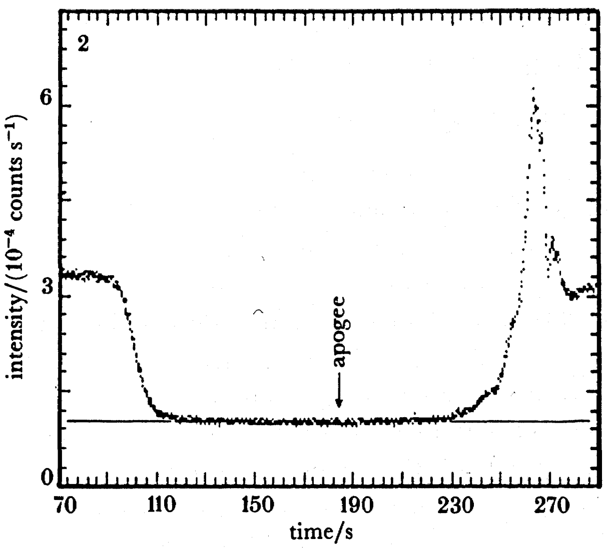


FIGURE 1. Oxygen-term diagrams and potential-energy curves identifying important transitions in the nightglow.

No particularly novel calibration technique has evolved in recent years and no new facility has become available to normalize calibrations internationally, possibly because the accepted attainable (although not necessarily achieved) limit of traditional methods of absolute calibration of 5–10% cannot, with assurance, be improved upon. One suspects that each laboratory believes it has the capability of calibrating within the above limits and the nature of nightglow variability is such that there are no grounds for supposing they are not successful in this respect.

Various means have been devised to satisfy the need for accurate attitude information. Attempted identification of stars, as they cross the photometer field of view, was employed on most of the early flights (Heppner & Meredith 1958; Tousey 1958). The usefulness of rocket-borne magnetometers was also exploited from an early stage, but magnetometers are limited in that they yield attitude only with respect to the magnetic vector and not absolute attitude with respect to the zenith. Murtagh *et al.* (1983) have shown how additional attitude information may be gleaned from the analysis of the modulation on the telemetry signal transmitted from a rotating dipole on the rocket and received by a polarized ground antenna, although such an arrangement may not always be logistically possible. Adopting published spectral and spatial characteristics of zodiacal and background star light, these authors then verified the magnetometer–aerial attitude by comparing the simulated with the measured sky-background components of the photometer signals. The availability of high quality and spectrally comprehensive measurements on background stars is increasing, and in conjunction with the more precise photometer systems in use today may now permit the direct computation of attitude of the required accuracy for the analysis of nightglow data; it certainly offers a very desirable second fix.

Radiant contamination of the photometer signals was first reported by Heppner & Meredith (1958) who, in valuable detail, described increases in intensity sufficient to saturate all their photometers during the descent of the rocket through the E-region. The extraneous glow was noted to be localized in the wake direction and to have an altitude dependence similar to that of the (upleg) Green Line emission at 557.7 nm. It was judged to result solely from reactions between atmospheric gases, precipitated by the immediate passage of the rocket. Other reports of similar contaminations were reviewed by Greer *et al.* (1983) in a preliminary discussion of the ETON project in which seven rockets were fired in quick succession in one night and a downleg luminous contamination was noted on every flight. The ETON project confirmed the spatial characteristics of the contamination broadly defined by Heppner & Meredith (1958) but increased its spectral extent from 275 nm to 1.6 μm, at least. Although many flight reports make no reference to a contaminating glow of any sort, the evidence is increasingly strong that the glow recorded from rockets in the lower thermosphere is likely to be the rule rather than the exception. It may be that only the severity varies from flight to flight. Tests for its occurrence lie in the observation of marked differences in the upleg–downleg data or unnatural deviations of the recorded integrated intensity from what might have been expected classically. Such differences are well illustrated in the recent ETON data (Greer *et al.* 1983) where the unambiguous upleg–downleg deviations (figure 2) permitted the confident identification of uncontaminated data on the upleg and, by substracting upleg from downleg, the separation of the downleg contamination component (figure 3). It can only be assumed that comparable tests are always rigorously applied before nightglow data are subjected to photochemical analysis.



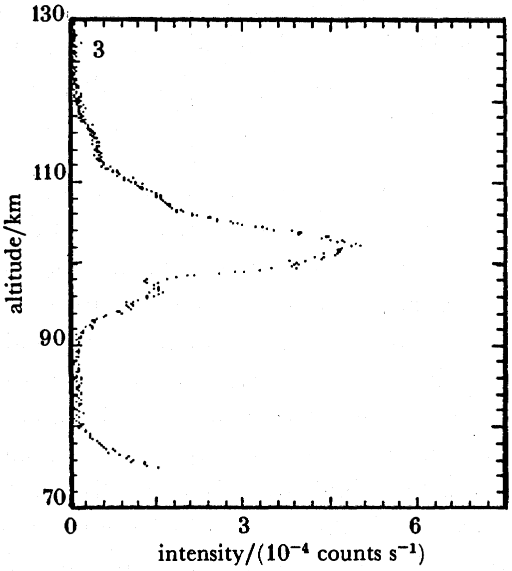


FIGURE 2. Total integrated measurement of 557.7 nm (P230H) showing pronounced differences between upleg and downleg signals: ETON data.

FIGURE 3. Downleg contamination at 557.7 nm (P230H) derived by subtracting upleg from downleg profiles: ETON data.

The different procedures for profile-fitting have been reviewed and evaluated by Murtagh *et al.* (1984). Although in different circumstances these methods each have their merits, Murtagh *et al.* conclude that the method of incremental straight-line fitting is generally to be preferred for the treatment of quality data because it has the capacity to delineate accurately the main features of the nightglow emission layer without necessarily obliterating structure of possible aeronomic significance, and it also preserves a measure of the probable error in the differentiation.

The extraction of unambiguous nightglow profiles from rocket photometer data is not a trivial exercise, and only the growing accord between the processed atmospheric data and photochemical models of the emission region justifies the belief that this exercise can now be accomplished reliably. As evidence of this, specific data relating to the Green Line and the Atmospheric Bands are now considered in some detail to indicate what we believe we know and how we have come to know it.

2. The O I Green Line at 557.7 nm

In the many rocket photometer studies of the lower thermosphere since 1955, the Green Line has been studied most frequently. The Green Line story has been succinctly reviewed by Bates (1978, 1981) but in tracing the contribution of *in situ* measurements to the development of our understanding of Green Line photochemistry it is necessary to revisit some of the past milestones.

The excitation mechanism for the ^1S state, as proposed by Chapman (1931), involved three-body collisions of neutral atomic oxygen

$$O + O + O \rightarrow O_2 + O(^1S) \quad [k_1]. \qquad (1)$$

Bates (1954) pointed out that such a three-body association can also lead to the formation of oxygen molecules in the $a^1\Delta_g$, $b^1\Sigma_g^+$, $A^3\Sigma_u^+$, $c^1\Sigma_u^-$ and $A'^3\Delta_u$ states, the latter two having been theoretically predicted, and that emissions from all these states should appear in the nightglow spectrum. Interestingly, Bates represented the Chapman mechanism as

$$(O+O)\, A^3\Sigma_u^+ + O(^3P) \rightarrow O_2(X^3\Sigma_g^-) + O(^1S), \qquad (2)$$

and noted the similarity to the ordinary transfer of electronic excitation.

Early rocket experiments designed to investigate the Green Line emission (Berg *et al.* 1956; Koomen *et al.* 1956) found the intensity peak to be located around 97 km and seemed to confirm Chapman's (1931) prediction with regard to height and his suggestion that reaction 1 was responsible. However, Krassovsky (1958) used this measured emission altitude together with a deduction, also based on rocket measurements (Friedman *et al.* 1951; Nicolet 1956), that atomic oxygen was concentrated mainly above 100 km, to challenge Chapman's mechanism and proposed instead an atom-interchange process that released $O(^1S)$ from vibrationally excited O_2. Krassovsky's alternative mechanism attracted little support and was subsequently rejected (Dalgarno 1958, 1963) for its inability to generate the measured Green Line intensity. Nevertheless, his unsuccessful attempt to combine rocket determinations of density and intensity and from these to draw conclusions regarding the excitation mechanism must register as the first attempt to do what would not be attempted again for another nineteen years (Slanger & Black 1977) but which would eventually prove most rewarding.

More extensive modelling of rocket measurements was at that time prohibited by deficiencies in our understanding of reaction schemes, including quenching, and associated kinetics. Indeed, these deficiencies have been a major obstacle to progress in modelling the thermospheric photochemistry since then. On the other hand, it may be noted that the now-accepted characteristics of the Green Line profile as an emission that increases rapidly from 90 km to a peak around 97 km and then tails off rather more slowly to disappear around 120 km, was determined experimentally as early as 1958 by Heppner & Meredith and confirmed by Packer (1961).

From an evaluation of k_1 (less than 8×10^{-38} cm^6 s^{-1}) from laboratory measurements by Barth & Hildebrandt (1961), Barth (1961) concluded that the Chapman mechanism was inadequate to explain the atmospheric obervations of the Green Line. Barth proposed instead that the O(^{1}S) was produced in a two-step reaction (frequently referred to as the Barth mechanism), involving oxygen recombination in the presence of any third body M followed by energy transfer from the excited molecular precursor O_2^*.

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

$$O_2^* + O \rightarrow O_2 + O(^1S). \tag{4}$$

The problem with the Chapman mechanism was simply that the determined value of k_1 was too low (by a factor of 10^3 or 10^4 according to Barth & Hildebrandt (1961)). However, this condemnation was not conclusive because the value of k_1 could only be inferred: reaction (1) could not be isolated and studied separately from quenching processes, the nature and extent of which were uncertain, particularly at atmospheric temperatures. The problem with the Barth mechanism was that it was dependent on an adequate supply of a suitably energetic precursor source O_2^*, the existence of which could only be assumed, and assumption favoured the $A^3\Sigma_u^+$ state as the only acceptable one to be identified in the nightglow in abundance. Neither the $a^1\Delta_g$ nor the $b^1\Sigma_g^+$ states were considered to be viable contenders at their low observed levels of vibrational development (figure 1).

For the next 15 years no further evidence was offered in support of Barth's mechanism. Instead, laboratory effort was directed to remeasuring k_1, the value of which was gradually revised upwards to 1.5×10^{-34} cm^6 s^{-1} (Young & Black 1966) and to 6.3×10^{-33} cm^6 s^{-1} (Felder & Young 1972). During this time, rocket measurements of the nightglow Green Line were used to generate oxygen densities by the routine application of the Chapman mechanism (Dandekar & Turtle 1971; Offermann & Drescher 1973; Kulkarni 1976). The results of these experiments were not discriminating with regard to the aptness of the adopted reaction schematic.

More significant was the work of Donahue *et al.* (1973) who favoured the Chapman mechanism for the determination of vertical distributions of atomic oxygen from the analysis of extensive Green Line observations from the *OGO* satellite. The resulting topside oxygen-profile gradients were noted to be inconsistent with the expected vertical oxygen flux. Donahue *et al.* (1973) did attempt, unsuccessfully, to correct the profile gradient by means of a Barth-type excitation mechanism for the Green Line; their failure in this respect was seen to justify the repudiation of Barth's requirement for the existence of a precursor state of excited molecular oxygen. 'No precursor of this sort has ever been discovered, nor is there any reason to suspect the existence of one from laboratory or theoretical argument': a very positively expressed view, which was subsequently shown to be unreasonable (Greer *et al.* 1981). Donahue *et al.* (1973)

then removed the gradient problem by using a Chapman model and manipulating the temperature dependence of the relevant rate constants. They adopted a value for $k_1 = 3.4 \times 10^{-34} \exp(790/T)$ cm^6 s^{-1} and cautioned that a positive activation energy would inhibit a satisfactory fit to their data.

Subsequently, Slanger & Black (1976) redetermined the production rate for $O(^1S)$ to be $1.4 \times 10^{-30} \exp(-650/T)$ cm^6 s^{-1}, although the high gas pressure in their experiment prevented unambiguous identification of the precise production mechanism involved. Mindful that this measurement represented a significant argument against the Chapman mechanism they (Slanger & Black 1977) then tested available kinetic parameters in their ability to model measured atmospheric profiles. For this purpose they employed the Green Line data from Donahue *et al.* (1973) and oxygen data from Dickinson *et al.* (1974) and from Scholz & Offermann (1974). Although these measurements were widely separated, both geographically and temporally, Slanger & Black persuasively demonstrated that only the Barth mechanism facilitated acceptable fitting; they additionally favoured the O_2^* precursor to be in the $A^3\Sigma_u^+$ state. The analysis, by Thomas *et al.* (1979), of a different data set, comprising nearby concurrent Green Line and oxygen profiles, strongly endorsed Slanger & Black's conclusion. The fact that this conclusion was thus shown not to be overly sensitive to the lack of simultaneity in the data employed by Slanger & Black, added to its credibility.

R. J. Thomas (1981) reported an analysis of a measurement of atomic oxygen and related airglows (which included the Green Line and the Herzberg I system) obtained by himself and Young (Thomas & Young 1981). This analysis concluded that the Chapman mechanism would only fit the Green Line data if k_1 had a temperature dependence of $\exp(3000/T)$. A similarly unusual, although numerically smaller, temperature dependence, $\exp(1400/T)$, had been obtained both by Thomas *et al.* (1979) and by Slanger & Black (1977). All these authors made such a temperature dependence unwelcome in that it was not easy to explain. R. J. Thomas reasoned that, in any case, such a strong temperature dependence was unlikely because observed changes in Green Line intensity (Donahue *et al.* 1973) did not appear to be of the magnitude expected for observed large changes in lower thermospheric temperature (Noxon 1978). However, such selective use of non-simultaneous data is uncompelling. Noxon did indeed report temperature variations of ±50 K in a night, but also noted that there is neither a simple nor a unique relation between fluctuations in nightglow intensity and those in rotational temperature in the presence of a gravity wave and that it may well be that the temperature fluctuations will be large while the corresponding intensity fluctuations are small. Notwithstanding, reported Green Line intensities range from less than 40 R (Murtagh & Witt 1987; Deans *et al.* 1976) to more than 400 R (Witt *et al.* 1984) and variations of more than a factor of three in a night have been observed by Takahashi *et al.* (1986) in association with a temperature change from 180 K to 230 K. The grounds for rejecting the Chapman mechanism solely on the basis of its suggested temperature dependence are, therefore, not strong.

The absence of the Green Line from the Venusian nightglow (Lawrence *et al.* 1977; Krasnopolsky 1978) was also used against Chapman. If, R. J. Thomas argued, the Chapman mechanism was important and was as fast as the derived values for k_1 would suggest, then it should give rise to a prominent emission in the Venusian atmosphere above the region where quenching of $O(^1S)$ by CO_2 is dominant. The Barth mechanism would produce no Green Line because the precursor, O_2^*, believed by R. J. Thomas to be either $O_2(c^1\Sigma_u^-)$ or $O_2(A'^3\Delta_u)$, exists only in the lowest vibrational level and is thus either not sufficiently energetic or resonant for excitation of $O(^1S)$ by transfer.

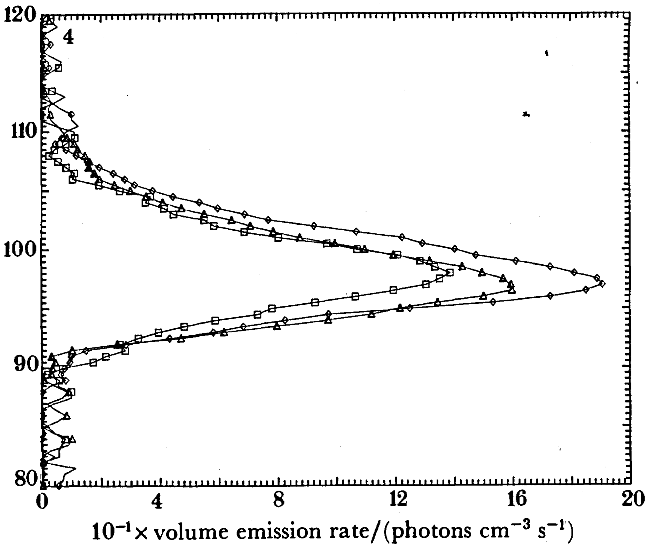
The case against $A^3\Sigma_u^+$ being the precursor state was based on the variation with altitude of the intensity ratio of Green Line to Herzberg I bands. R. J. Thomas represented this ratio in terms of a quenching factor Q_S for $O(^1S)$ and calculated that his own data would require Q_S to increase by a factor of 2 from 94 to 105 km through the region of maximum Green Line emission. This, as R. J. Thomas noted, was not sensible, and was therefore inconsistent with $A^3\Sigma_u^+$ being the precursor state. The same exercise applied to the data of Thomas *et al.* (1979) indicated that Q_S would remain essentially constant with altitude from 90 to 110 km. R. J. Thomas allowed this to be possible only if $O(^1S)$ is not quenched in this altitude region by O and, as he had assumed the opposite, he was again persuaded against the $A^3\Sigma_u^+$ state. The discovery (Slanger & Black 1981) that $O(^1S)$ is indeed not quenched by O, but rather by $O_2(^1\Delta_g)$, vitiates the R. J. Thomas argument and the case against the $A^3\Sigma_u^+$ state is therefore not proven by his analysis.

In an examination of the total Green Line quenching, R. J. Thomas implied that the greater portion relates to quenching of the precursor O_2^* and, of that portion, most is radiative. It follows that because the precursor must be produced in abundance to maintain the Green Line emission, it should also itself be prominent in emission. Such a conclusion is at odds with R. J. Thomas's belief that the precursor state is either $A'^3\Delta_u$ or $c^1\Sigma_u^-$, both of which are known to be excited, although their emissions are weak, in the nightglow (Chamberlain 1961; Slanger & Huestis 1981).

It should be noted that the nightglow data as presented by R. J. Thomas are rather non-standard. The upleg Green Line profile rises remarkably quickly from close to zero emission at about 93 km to a peak below 95 km, whereas the downleg profile is either double peaked or strongly modulated. These peculiarities and differences are not commented on, but may evidence radiative contamination of the observations, similar to that believed to have destroyed the downleg Herzberg I data (Thomas & Young 1981). If this is the case, it may be that the quality of the data does not match the inventiveness of the analysis.

The ETON campaign (Greer *et al.* 1986), which was conducted from S. Uist, Scotland, involved the flight, within a period of 2.5 h, of seven rockets, five of which carried nightglow photometers. A total of eighteen photometers measured most of the prominent oxygen features, as can be seen from table 1, and the Green Line was measured three times. The latter three profiles, reproduced in figure 4, all derive from upleg data because, as noted earlier, all downleg data was radiatively contaminated to varying degrees. The extent to which the profile shape in figure 4 is maintained from flight to flight, with the only significant difference, that between intensities, seeming to correlate with changes in the oxygen density (figures 6 and 7) strongly indicates that the Green Line profiles are contamination free.

The analysis of these profiles (McDade *et al.* 1986) indicated that the Green Line intensity did not follow an $[O]^3$ dependence and that, as before, a Chapman mechanism could only be tolerated if the production rate coefficient k_1 is strongly temperature dependent. Adopting a Barth energy-transfer mechanism and following the approach of R. J. Thomas (1981), McDade *et al.* (1986) then extensively examined the requirements for quenching of the $O(^1S)$ precursor, O_2^*. From a detailed photochemical model, which embraced the Green Line intensity and the temporally interpolated atomic oxygen density, a quenching expression was developed for the precursor that permitted the resolution of the effects of quenching by radiation, by O_2 and by O. Simultaneous least-squares fitting of the set of quenching profiles to O_2 (from either CIRA 1972 or MSIS-83 (Hedin 1983)) and the set of interpolated atomic oxygen profiles, yielded fitting coefficients for the three quenching effects. In contradiction of the findings of



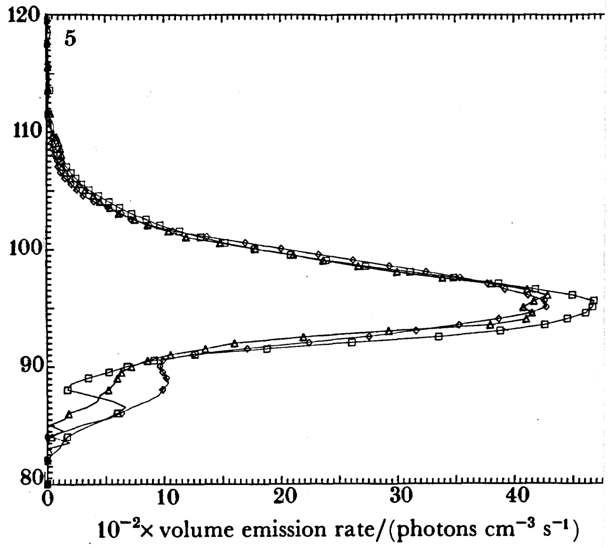


FIGURE 4. Nightglow profiles of the O(^{1}S) Green Line: ETON data. Symbols: △, P229H, 557.7 nm; □, P230H, 557.7 nm; ◇, P231H, 557.7 nm.

FIGURE 5. Nightglow profiles of the (0, 0) band in the $O_2(b^1\Sigma_g^+)$ Atmospheric system: ETON data. Symbols: △, P227H, 761.9 nm; □, P229H, 761.9 nm; ◇, P230H, 761.9 nm.

TABLE 1. DEPLOYMENT OF EXPERIMENTS AND PAYLOADS IN THE ETON CAMPAIGN, 23 MARCH 1982, SOUTH UIST, SCOTLAND

rocket	measurement	source	IOF (UT) h:min:s	firing sequence Δ IOF h:min:s	Σ(Δ IOF) h:min:s
P230H	320 nm: $O_2(A^3\Sigma_u^+)$ Herz. I	Q.U.B.	21:27:17	00:00:00	00:00:00
	540 nm: Continuum	Q.U.B.			
	557.7 nm: O(^{1}S) Green Line	Q.U.B.			
	761.9 nm: $O_2(b^1\Sigma_g^+)$ Atmos.	Q.U.B.			
P232H	atomic oxygen concentration	R.A.L.	21:48:41	00:21:24	00:21:24
	electron density	R.A.L.			
	temperature	U.C.W.			
P227H	320 nm: $O_2(A^3\Sigma_u^+)$ Herz. I	Q.U.B.	22:10:51	00:22:10	00:43:34
	761.9 nm: $O_2(b^1\Sigma_g^+)$ Atmos.	Q.U.B.			
	1.27 µm: $O_2(a^1\Delta_g)$ IR Atmos.	I.S.A.S.			
	temperature	U.C.W.			
P229H	330 nm: $O_2(A^3\Sigma_u^+)$ Herz. I	M.I.S.U.	22:57:55	00:47:04	01:30:38
	370 nm: $O_2(A'^3\Delta_u)$ Chamb.	M.I.S.U.			
	557.7 nm: O(^{1}S) Green Line	M.I.S.U.			
	761.9 nm: $O_2(b^1\Sigma_g^+)$ Atmos.	M.I.S.U.			
P231H	275 nm: $O_2(A^3\Sigma_u^+)$ Herz. I	Q.U.B.	23:12:59	00:15:04	01:45:42
	320 nm: $O_2(A^3\Sigma_u^+)$ Herz. I	Q.U.B.			
	540 nm: Continuum	Q.U.B.			
	557.7 nm: O(^{1}S) Green Line	Q.U.B.			
P228H	714 nm: Continuum	Q.U.B.	23:28:23	00:15:24	02:01:06
	724 nm: OH(8–3) band	Q.U.B.			
	1.61 µm: OH($\Delta v = 2$ sequence)	I.S.A.S.			
	temperature	U.C.W.			
P234H	atomic oxygen concentration	R.A.L.	23:55:15	00:26:52	02:27:58
	electron density	R.A.L.			
	temperature	U.C.W.			

Abbreviations: Q.U.B., The Queen's University of Belfast (U.K.); R.A.L., The Rutherford Appleton Laboratory (U.K.); U.C.W., The University College of Wales, Aberystwyth; M.I.S.U., The Meteorological Institute of Stockholm University; I.S.A.S., The Institute for Space and Atmospheric Science (Saskatoon).

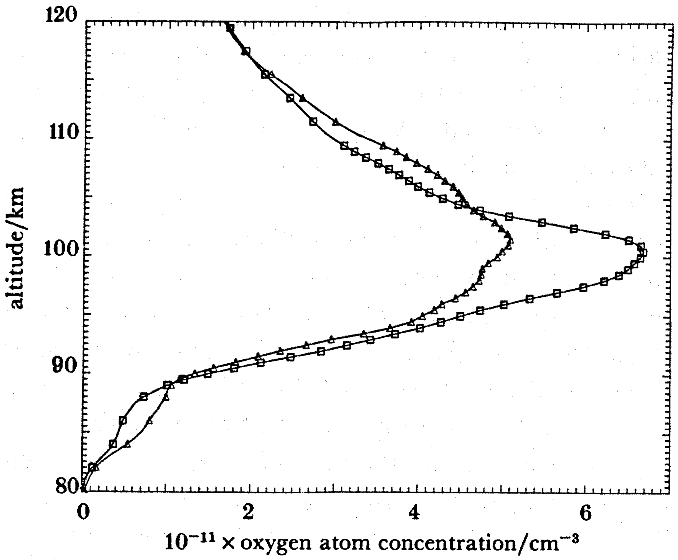


FIGURE 6. Night-time profiles of the measured atomic oxygen concentration: ETON data. Symbols: △, P232H; □, P234H.

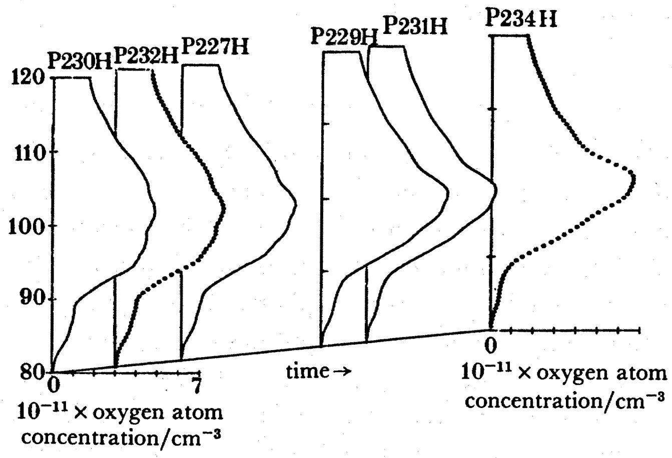


FIGURE 7. Atomic oxygen profiles measured on ETON flights P232H and P234H (dotted curves) and the profiles interpolated for the times of other flights (solid curves).

R. J. Thomas (1981), McDade *et al.* concluded that spontaneous emission makes only a minor contribution to precursor loss at the Green Line peak, although the upper limits on this radiation are not so small as to automatically preclude any of the three ($c^1\Sigma_u^-$, $A'^3\Delta_u$, $A^3\Sigma_u^+$) excited states of O_2 from being the precursor; they deduced that the production efficiency of the $O(^1S)$ precursor must be at least 0.45–0.55%.

The fitting coefficients for quenching by O_2 and O were, of course, functions of the input parameters, Green Line intensity and interpolated atomic oxygen profiles, the latter being used because oxygen was not measured directly on any of the Green Line flights. As a demonstration of the efficacy of these coefficients, they were used to regenerate the Green Line profile, which was then compared with the measured version. Some deviation in this match persuaded McDade *et al.* (1986) to alternatively derive oxygen profiles from the inversion of the O_2

Atmospheric Band profiles (figure 5) that were simultaneously measured on two of the Green Line flights. A recomputation of the quenching coefficients led to a considerably improved fit with the measurements (figure 8). It is clearly one of the strengths of the ETON project that the wealth of data it produced has facilitated a valuable cross correlation of measurements and consequent increased confidence in derived parameters.

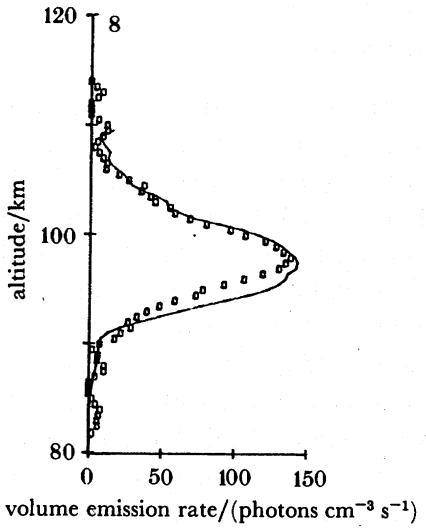
The values of the coefficients for quenching of the Green Line precursor by O_2 and by O were computed by McDade *et al.* for different model atmospheres and different derived O profiles. These coefficients indicated dominant quenching of the precursor by O above 95 km. The apparent contradiction with the work of R. J. Thomas (1981), who concluded that quenching by O_2 was dominant, is suggested by McDade *et al.* (1986) to result from the relatively constant oxygen profile that R. J. Thomas obtained over the Green Line region. Such a constant oxygen profile prevents its quenching effect from being resolved from radiative loss.

Finally, McDade *et al.* (1986) showed that the ratio of the quenching coefficients by O and O_2 (approximately 20), is not comparable with laboratory ratios derived for the $A^3\Sigma_u^+$ and $c^1\Sigma_u^-$ states, which are 80 ± 10 and 200 ± 20, respectively. The important point was made that the laboratory ratios are pertinent to specific vibrational levels (all low) whereas the significance of vibrational excitation of the precursor in the atmosphere is unknown. This may explain the differences in the above ratios. It is also a primary reason why, from the ETON results, the identity of the $O(^1S)$ precursor in the nightglow cannot yet be confirmed.

3. THE ATMOSPHERIC BAND SYSTEM AT 761.9 nm

The transition $O_2(b^1\Sigma_g^+ - X^3\Sigma_g^-)$ gives rise to both the (0, 0) band at 761.9 nm and the (0, 1) band at 864.5 nm of the Atmospheric system of molecular oxygen in the nightglow. Although the (0, 0) band, which has a measured intensity of several kilorayleighs, is the more intense by a factor of about 17 (Wallace & Hunten 1968), it is totally absorbed in the lower atmosphere and therefore can only be studied from altitudes above 60 km with rocket-borne instrumentation. With few exceptions, the volume emission profiles of the Atmospheric Bands that have been reported (Packer 1961; Tarasova 1963; Deans *et al.* 1976; Witt *et al.* 1979, 1984; Watanabe *et al.* 1981; Harris 1983; Greer *et al.* 1986), agree that the altitude of maximum emission is at 94 ± 1 km and significantly, in terms of the photochemistry, below that of the Green Line. Profiles of the Atmospheric Band measured by Greer *et al.* (1986) are shown in figure 5 and may be compared with the Green Line profiles in figure 4. The measurement by Tarasova (1963) that shows an emission peak at 80 km cannot be reconciled with any known or proposed excitation mechanism, and the possibility exists that the measurement of a peak at 91 km by Deans *et al.* (1976) may have been influenced by auroral contamination.

Deans *et al.* (1976) used their measured profile at 761.9 nm to generate oxygen densities by assuming that $O_2(b^1\Sigma_g^+)$ was produced directly in the three-body recombination, reaction (3). Apart from the difficulty of coping with an auroral presence, they had no concurrent measurement of atomic oxygen and their results, which they favourably compared with the oxygen densities of Donahue (1973), can therefore only be termed inconclusive. A rocket experiment by Witt *et al.* (1979), in which they measured the Atmospheric Band, the Green Line and the OH(8–3) Meinel band, enabled them to perform a similar exercise. The disparity between oxygen profiles derived from both the Atmospheric Band and Green Line profiles led them to conclude that reaction (3) was not the major source of $O_2(b^1\Sigma_g^+)$ in the nightglow. Prompted



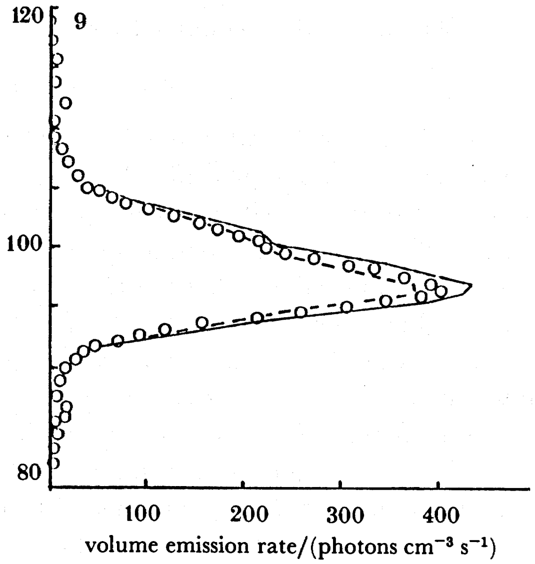


FIGURE 8. Measured Green Line emission profile (open symbols) and the matched profile (solid line) generated by using oxygen data derived from inversion of the Atmospheric Band: ETON data (P230H).

FIGURE 9. Measured OASIS Green Line emission profile (○) and matched profiles generated from oxygen data derived from inversion of the OASIS Atmospheric Band but with ETON quenching coefficients. Solid line, $k = 8 \times 10^{-14}$ cm^3 s^{-1}; broken line, $k = 0$.

by Slanger & Black's (1977) convincing argument in favour of indirect excitation for O(^{1}S) and the analysis of Llewellyn & Solheim (1978) (which indicated that rocket observations of the infrared Atmospheric Band at 1.27 μm cannot be satisfactorily explained by direct recombination of atomic oxygen), Witt *et al.* (1979) considered the excitation of the $b^1\Sigma_g^+$ state through vibrationally excited hydroxyl

$$\mathrm{OH}^*(v > 4) + \mathrm{O} \rightarrow \mathrm{O_2}(b^1\Sigma_g^+) + \mathrm{H}. \qquad (5)$$

Employing an atomic oxygen profile from Dickinson *et al.* (1974), Witt *et al.* (1979) constructed an $O_2(b^1\Sigma_g^+)$ profile from reaction (5). Comparison with the measured Atmospheric Band showed limited agreement, on the basis of which they asserted that the OH* source provided by reaction (5) was potentially significant.

Watanabe *et al.* (1981) also analysed their Atmospheric Band measurements by a direct recombination method (reaction (3)), and also used the Dickinson *et al.* (1974) profile as the best available oxygen data; their comparison of calculated and measured emission profiles displayed disturbing disparity, particularly on the bottom side, which they attributed to experimental error.

In 1979, Llewellyn *et al.* considered the excitation mechanism of the Herzberg I system in some detail and persuasively argued that energy transfer from an excited precursor was probably involved. Subsequently, Greer *et al.* (1981) considered the viability of this idea for the $b^1\Sigma_g^+$ state. From an extensive literature search they concluded that substantial evidence already existed that supported such a suggestion and that even pointed to O_2 being the transfer agent. The studies of Trajmar *et al.* (1972) and Lawton & Phelps (1978) seemed to cast $O_2(c^1\Sigma_u^-)$ in the role of precursor to $O_2(b^1\Sigma_g^+)$ and the identification of the $c^1\Sigma_u^-$ state as a prominent product of oxygen association in the Venusian atmosphere (Lawrence *et al.* 1977) and in a laboratory afterglow (Slanger 1978) encouraged Greer *et al.* (1981) to propose

$$O_2(c^1\Sigma_u^-) + O_2 \rightarrow O_2(b^1\Sigma_g^+) + O_2. \tag{6}$$

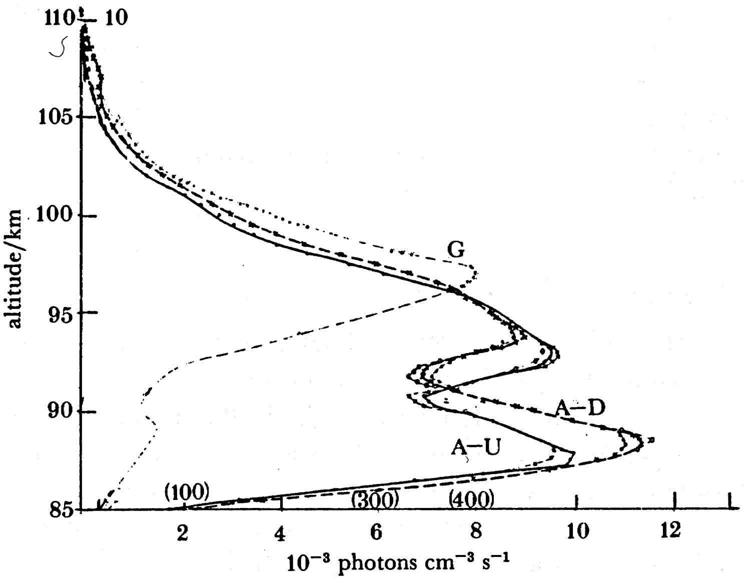
The relative absence of the Atmospheric Band from the Venusian nightglow was to be expected because of its known rapid quenching by CO_2 (Aviles *et al.* 1980). The fact that only the $v' = 0$ progressions were developed on Venus was not seen as a problem because this vibrational level for the $c^1\Sigma_u^-$ state could populate up to the $v' = 5$ level of the $b^1\Sigma_g^+$ state. The confirmation by Slanger & Huestis (1981) that the Herzberg II emission is indeed weakly developed in the terrestrial nightglow up to $v' = 7$ (which dominates) and the subsequent observation by Ogryzlo *et al.* (1984) that the production of the Atmospheric Band during oxygen recombination is best described by a transfer mechanism and that $O_2(c^1\Sigma_u^-)$ could only be the precursor if it was in other than the lowest vibrational levels, is not inconsistent with reaction (6).

Witt *et al.* (1984) reported measurements of the Atmospheric Band that have important implications for our better understanding of the photochemistry. They describe the results and analysis of one measurement from rocket S35, fired from Esrange, Sweden, and the preliminary analysis of one of the measurements obtained during the ETON campaign (Greer *et al.* 1986). The full analysis has been detailed by McDade *et al.* (1986), particularly with reference to the quenching parameters of the proposed precursor. Although there is some overlap between the two papers, for clarity Witt *et al.* (1984) will be considered only with regard to S35.

S35 was fired during an intense stratospheric warming event and on a geomagnetically quiet night within a disturbed period. The photometer measurements, which included the Atmospheric Band and the Green Line, were preceded by an oxygen density measurement (resonance fluorescence) seventeen minutes earlier. Figures 10 and 11 illustrate both the emission profiles and the oxygen profile obtained. Unusually, the latter profile features a pronounced double peak with a very abrupt cut-off on the bottom side. The relative prominence of this peculiarity in the Atmospheric Band profiles enforces the belief that the transfer agent from the precursor to the $b^1\Sigma_g^+$ state is a molecular species.

McDade *et al.* (1986) developed a detailed photochemical model by which they could analyse the measured (ETON) Atmospheric Band and oxygen profiles either on the basis of direct excitation or indirectly through an energy transfer step. In the direct excitation model the efficiency of production, ϵ, of $O_2(b^1\Sigma_g^+)$ is expressed in terms of known or measured parameters and shown to be strongly altitude dependent (figure 12). This dependence is unacceptable, unless ϵ is strongly temperature dependent, and rules against the direct process of excitation. In the indirect excitation model, McDade *et al.* (1986) concentrated on the precursor loss rate, Q_A, which they expressed in terms of the individual quenching effects of O, O_2 and N_2 and which they evaluated, as a total quenching effect, from observed emission rates and a model atmosphere. For the ETON project, the latter model included oxygen profiles interpolated, from those measured, to coincide temporally with the emission measurement (figure 7). The altitude profile of the evaluated total quenching is shown in figure 13 and clearly exhibits the form expected of a transfer mechanism.

The exercise of fitting the formulation of Q_A to the evaluated quenching profile permitted the determination of the relative coefficients for quenching of the precursor by O and O_2; the scale heights of O_2 and N_2 were too similar to allow *their* quenching effects to be resolved. Results are illustrated in figure 13 and from the goodness of fit alone are supportive of the transfer



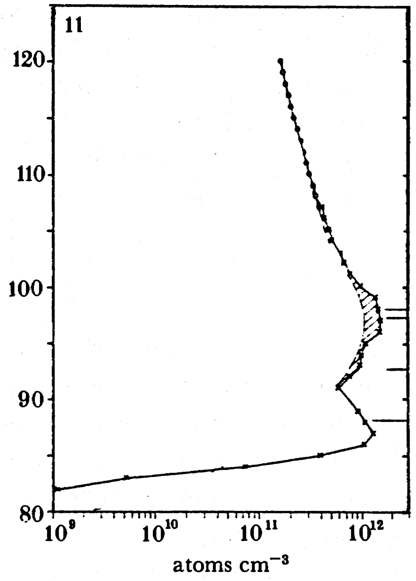
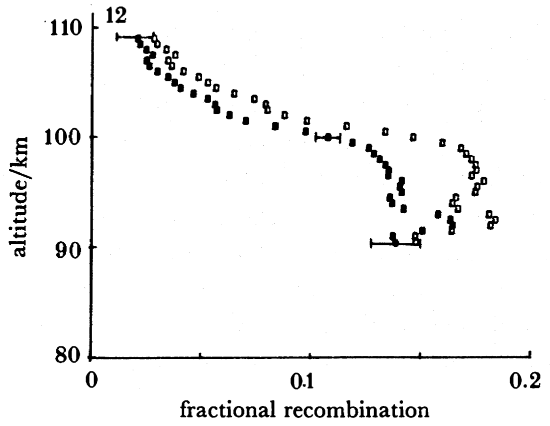


Figure 10. Measured Atmospheric Band upleg (A–U) and downleg (A–D) profiles with simultaneous Green Line profile: S35 data.

Figure 11. Atomic oxygen profile measured in association with S35.



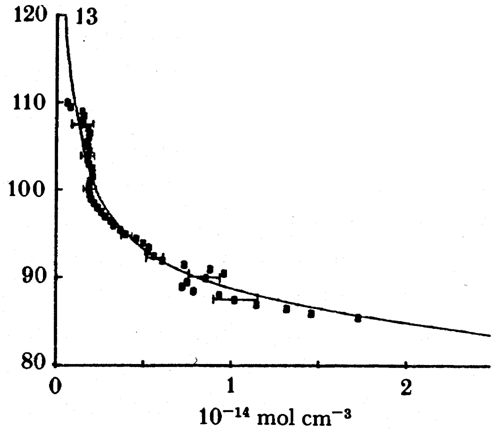


Figure 12. Efficiency of production of $O_2(b^1\Sigma_g^+)$ in an assumed direct recombination process for $k = 0$ (solid dots) and $k = 8 \times 10^{-14}$ (open dots), where k relates to quenching of $O_2(b^1\Sigma_g^+)$ by O.

Figure 13. Altitude profile of total quenching of the $O_2(b^1\Sigma_g^+)$ precursor (dots) with model fit.

model. The results suggest in fact that radiative quenching of the precursor accounts for less than 10 % of its loss at the Atmospheric Band intensity peak and that quenching by O is between 2 and 5 times more effective than quenching by O_2.

The validity of the derived quenching coefficients, and the transfer model generally, was rigorously tested in relation to a quite separate rocket-photometer investigation of the nightglow. This investigation included Atmospheric Band and Green Line profiles recorded simultaneously in 1983 at White Sands, New Mexico, during the project OASIS. The Atmospheric Band measurement (Harris 1983) was inverted, by using the McDade *et al.* (1986)

quenching coefficients, to derive atomic oxygen densities that were then used in a Barth-type mechanism to generate a Green Line profile. Bearing in mind that the OASIS Green Line intensity was about twice that measured in ETON the resulting agreement, evident in figure 9, is compelling. The two Green Line profiles shown were computed corresponding to the limiting values, determined by Slanger & Black (1979), for the quenching rate, k, of $O_2(b^1\Sigma_g^+)$ by O; $k = 0$ and $k = 8\times10^{-14}$ cm^3 s^{-1}. The model and quenching parameters have faithfully reproduced the emission profile: even the inflection on the top-side.

4. CONCLUDING REMARKS

In situ measurements of the lower thermospheric nightglow and associated modelling have valuably contributed to our better understanding of the oxygen photochemistry of that region. It now seems probable that both the Green Line and the Atmospheric Band emissions in the nightglow are excited through energy transfer. Such mechanisms can apparently be modelled to accommodate satisfactorily the shape of the emission profile and its variation with time and geographic location. There is evidence, from the analysis of volume emission profiles, that $O_2(b^1\Sigma_g^+)$ and $O(^1S)$ may not have the same precursor because each appears to be quenched by O_2 and O at different rates. If the precursors to the Atmospheric Band and the Green Line *are* different, they may be different only in terms of the vibrational levels from which they transfer. The consequences of vibrational development of electronically excited states of O_2 for both laboratory and atmospheric measurements and the inter-relations between them is still uncertain but the evidence (Ogryzlo *et al.* 1984; McDade *et al.* 1986) would suggest that vibrational excitation must increase the transfer efficiencies from precursors.

The $^5\Pi_g$ state of O_2 (figure 1), promoted by Wraight (1982) as the likely product, albeit weakly bound, in over 70% of oxygen atom recombinations at temperatures below 200 K, may yet be shown to play an important part in energy transfer mechanisms either as a short-lived initiator of precursor production or as a precursor itself (Wayne 1984). However, Smith (1984) has cautioned that the $^5\Pi_g$ state may be *so* weakly bound that it dissociates thermally before being electronically quenched. Krasnopolsky (1986) has argued that the $^5\Pi_g$ state is the mother precursor to all excited states of O_2 and also $O(^1S)$! Rocket-photometer measurements of nightglow emission profiles cannot yet comment definitively on these possibilities, but it is more than likely that further detailed *in situ* measurements still have a critical part to play in our developing understanding of the problem.

REFERENCES

Aviles, R. G., Muller, D. F. & Houston, P. L. 1980 *Appl. Phys. Lett.* **37**, 358–360.
Barth, C. A. 1961 *Science, Wash.* **134**, 1426.
Barth, C. A. & Hildebrandt, A. F. 1961 *J. geophys. Res.* **66**, 985–986.
Bates, D. R. 1954 In *The Earth as a planet* (ed. G. P. Kuiper), pp. 576–643. University of Chicago Press.
Bates, D. R. 1978 *Planet. Space Sci.* **26**, 897–912.
Bates, D. R. 1981 *Planet. Space Sci.* **29**, 1061–1067.
Berg, O. E., Koomen, M., Meredith, L. & Scolnik, R. 1956 *J. geophys. Res.* **61**, 302–303.
Broadfoot, A. L. & Kendall, K. R. 1968 *J. geophys. Res.* **73**, 426–428.
Chamberlain, J. W. 1961 *Ann. Geophys.* **17**, 201.
Chapman, S. 1931 *Proc. R. Soc. Lond.* A **132**, 353–374.
CIRA 1972 *COSPAR International Reference Atmosphere.* Berlin: Akademie-Verlag.
Dalgarno, A. 1958 *Ann. Geophys.* **14**, 241–252.

Dalgarno, A. 1963 *Planet. Space Sci.* **10**, 19–28.
Dandekar, B. S. & Turtle, J. P. 1971 *Planet. Space Sci.* **19**, 949–957.
Deans, A. J., Shepherd, G. G. & Evans, W. F. J. 1976 *Geophys. Res. Lett.* **3**, 441–444.
Dickinson, P. H. G., Bolden, R. C. & Young, R. A. 1974 *Nature, Lond.* **252**, 289–291.
Donahue, T. M., Guenther, B. & Thomas, R. J. 1973 *J. geophys. Res.* **78**, 6662–6689.
Felder, W. & Young, R. A. 1972 *J. chem. Phys.* **56**, 6028–6030.
Friedman, H., Lichtman, S. W. & Byram, E. T. 1951 *Phys. Rev.* **83**, 1025–1030.
Greer, R. G. H., Llewellyn, E. J., Solheim, B. H. & Witt, G. 1981 *Planet. Space Sci.* **29**, 383–389.
Greer, R. G. H., Murtagh, D. P., Witt, G. & Stegman, J. 1983 In *Sixth ESA Symp. Sound. Rockets and Balloons, Interlaken* (ESA SP-183) (ed. E. Kopp), pp. 341–347. Noordwijk, Netherlands: European Space Agency.
Greer, R. G. H., Murtagh, D. P., McDade, I. C., Dickinson, P. H. G., Thomas, L., Jenkins, D. B., Stegman, J., Llewellyn, E. J., Witt, G., Mackinnon, D. J. & Williams, E. R. 1986 *Planet. Space Sci.* **34**, 771–788.
Harris, F. R. 1983 *Eos. Wash.* **64**, 799.
Hedin, A. E. 1983 *J. geophys. Res.* **88**, 10170–10188.
Heppner, J. P. & Meredith, L. H. 1958 *J. geophys. Res.* **63**, 51–65.
Koomen, M., Scolnik, R. & Tousey, R. 1956 *J. geophys. Res.* **61**, 304–306.
Krasnopolsky, V. A. 1978 *Cosmic Res.* **16**, 895–903.
Krasnopolsky, V. A. 1986 *Planet. Space Sci.* **34**, 511–518.
Krassovsky, V. I. 1958 *Ann. Geophys.* **14**, 395–413.
Krassovsky, V. I., Shefov, N. N. & Yarin, V. I. 1962 *Planet. Space Sci.* **9**, 883–915.
Kulkarni, P. V. 1976 *J. geophys. Res.* **81**, 3740–3744.
Lawrence, G. M., Barth, C. A. & Argabright, V. 1977 *Science, Wash.* **195**, 573–574.
Lawton, S. A. & Phelps, A. V. 1978 *J. chem. Phys.* **69**, 1055–1068.
Llewellyn, E. J. & Solheim, B. H. 1978 *Planet. Space Sci.* **26**, 533–538.
Llewellyn, E. J., Solheim, B. H., Stegman, J. & Witt, G. 1979 *Planet. Space Sci.* **27**, 1507–1511.
McDade, I. C., Murtagh, D. P., Greer, R. G. H., Dickinson, P. H. G., Witt, G., Stegman, J., Llewellyn, E. J., Thomas, L. & Jenkins, D. B. 1986 *Planet. Space Sci.* **34**, 789–800.
Murtagh, D. P., Greer, R. G. H. & McDade, I. C. 1983 In *Sixth ESA Symp. Sound. Rockets and Balloons, Interlaken* (ed. E. Kopp), pp. 365–369. European Space Agency.
Murtagh, D. P., Greer, R. G. H., McDade, I. C., Llewellyn, E. J. & Bantle, M. 1984 *Ann. Geophysicae* **2**, 467–474.
Murtagh, D. P. & Witt, G. 1987 In *Proc. XIV Annual Meeting of Atmospheric Studies by Optical Methods, Cambridge, U.K.* (ed. M. J. Rycroft). (In the press.)
Nicolet, M. 1956 In *Rocket exploration of upper atmosphere* (ed. R. L. F. Boyd & M. J. Seaton), pp. 357. Oxford: Pergamon Press.
Noxon, J. F. 1978 *Geophy. Res. Lett.* **5**, 25–27.
Offermann, D. & Drescher, A. 1973 *J. geophys. Res.* **78**, 6690–6700.
Ogryzlo, E. A., Shen, Y. Q. & Wassell, P. T. 1984 *J. Photochem.* **25**, 389–399.
Packer, D. M. 1961 *Ann. Geophys.* **17**, 67–75.
Scholz, T. G. & Offermann, D. 1974 *J. geophys. Res.* **79**, 307–310.
Slanger, T. G. 1978 *J. chem. Phys.* **69**, 4779–4791.
Slanger, T. G. & Black, G. 1976 *J. chem. Phys.* **64**, 3767–3773.
Slanger, T. G. & Black, G. 1977 *Planet. Space Sci.* **25**, 79–88.
Slanger, T. G. & Black, G. 1979 *J. chem. Phys.* **70**, 3434–3438.
Slanger, T. G. & Black, G. 1981 *J. Photochem.* **17**, 122.
Slanger, T. G. & Huestis, D. L. 1981 *J. geophys. Res.* **86**, 3551–3554.
Smith, I. W. M. 1984 *Int. J. chem. Kinetics* **16**, 423–443.
Takahashi, H., Sahai, Y. & Batista, P. P. 1986 *Planet. Space Sci.* **34**, 301–306.
Tarasova, T. M. 1963 In *Space research III* (*COSPAR*) (ed. W. Priester), pp. 162–172. Amsterdam: North-Holland.
Thomas, L., Greer, R. G. H. & Dickinson, P. H. G. 1979 *Planet. Space Sci.* **27**, 925–931.
Thomas, R. J. 1981 *J. geophys. Res.* **86**, 206–210.
Thomas, R. J. & Young, R. A. 1981 *J. geophys. Res.* **86**, 7389–7393.
Tousey, R. 1958 *Ann. Geophys.* **14**, 186–195.
Trajmar, S., Williams, W. & Kuppermann, A. 1972 *J. chem. Phys.* **56**, 3759–3765.
Wallace, L. & Hunten, D. M. 1968 *J. geophys. Res.* **73**, 4813–4834.
Watanabe, T., Nakamura, M. & Ogawa, T. 1981 *J. geophys. Res.* **86**, 5768–5774.
Wayne, R. P. 1984 *J. Photochem.* **25**, 345–364.
Witt, G., Stegman, J., Solheim, B. & Llewellyn, E. J. 1979 *Planet. Space Sci.* **27**, 341–350.
Witt, G., Stegman, J., Murtagh, D. P., McDade, I. C., Greer, R. G. H., Dickinson, P. H. G. & Jenkins, D. B. 1984 *J. Photochem.* **25**, 365–378.
Wraight, P. 1982 *Planet. Space Sci.* **30**, 251–259.
Young, R. A. & Black, G. 1966 *J. chem. Phys.* **44**, 3741–3751.

Discussion

B. A. Thrush, F.R.S. I. P. Stott and I have been studying the oxygen airglow in the laboratory in an attempt to identify or eliminate different highly excited states of O_2 as the precursors of $O(^1S)$ in the Barth mechanism.

In our work, oxygen atoms are generated by a microwave discharge through 1–2 % oxygen in a flowing argon carrier at total pressures between 5 and 10 Torr (*ca.* 660–1220 Pa). The inert carrier is needed to prevent loss of active species on the vessel walls. Emissions are observed with a computer-controlled monochromator and sensitive photomultiplier. The emissions by O_2, $A^3\Sigma_u^+$ ($v = 0$–8), O_2, $A'^3\Delta_u$ ($v = 2, 3, 4$) and $O(^1S)$ are observed. On addition of carbon dioxide the emission by O_2A is strongly quenched but that by O_2, $c^1\Sigma_u$ ($v = 0$) is greatly enhanced, showing that collisions with CO_2 produce the efficient conversion of O_2A to O_2c. This is in agreement with observations of strong emission by the latter but not by the former in the atmosphere of Venus.

In our system, an added quenching agent (X) must quench emission by $O(^1S)$ more strongly than it quenches emission by the precursor (P) of $O(^1S)$ because the quencher can act both on P and on $O(^1S)$. If we represent the other quenchers already present as Q, the basis reaction mechanism is:

$$O+O+M \rightarrow\rightarrow P+M,$$

$$O+P = O(^1S)+O_2, \qquad (1)$$

$$O(^1S) = O(^1D)+h\nu, \qquad A_{nm}.$$

$$O(^1S)+Q = O+Q, \qquad (2)$$

$$O(^1S)+X = O+X, \qquad (3)$$

$$P+Q = O_2+Q, \qquad (4)$$

$$P+X = O_2+X, \qquad (5)$$

$$P = O_2+h\nu. \qquad (6)$$

This yields a Stern–Volmer equation of the form

$$\frac{I_0(^1S)}{I(^1S)} = \frac{I_0(P)}{I(P)}\left(1+\frac{k_3[X]}{\sum_Q k_2[Q]+A_{nm}}\right).$$

Stern–Volmer plots of I_0/I for emission by $O(^1S)$ and by the observed states of O_2 have been made for $X = CO_2$, O_2 and SF_6. On this basis we can eliminate all the observed levels of O_2 except O_2, $A^3\Sigma_u^+$ ($v \geqslant 6$) as precursors of $O(^1S)$ in the Barth mechanism.

S. A. Bowhill. Dr Greer mentioned that he was attributing gravity-wave-induced fluctuations in Green Line intensity to temperature fluctuations. Is it not more likely that they are caused by density fluctuations arising from the vertical wave motion?

R. G. H. Greer. I agree with Professor Bowhill's latter point. However, I hope I did not attribute the gravity-wave-induced fluctuations in Green Line intensity to temperature fluctuations. I mentioned that, for an assumed Chapman mechanism, clear evidence for the apparent strong temperature dependence of the production-rate coefficient for O(^{1}S) was missing from ground-based intensity measurements. I also noted that related density and temperature fluctuations arising from the passage of a vertical wave may act to minimize or disguise associated intensity fluctuations. In the ETON project, temperature profiles were not successfully monitored and so vertical wave propagation was not investigated further. For this reason we applied a linear extrapolation in time to the measurements of atomic oxygen density to produce oxygen profiles appropriate to the separately measured Green Line intensities.