Cause of Terrestrial Nightglow Continuum

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Since the nightglow's green continuum was discovered over 40 years ago the theory that it arises from the NO_2 air afterglow has been generally accepted so that its intensity is regarded as a useful measure of the abundance of nitric oxide in the lower thermosphere. This theory is shown to be untenable. Observational evidence points unambiguously to a novel source: metastable oxygen molecules colliding with ambient gas molecules and thereby forming complexes that dissociate by allowed radiative transitions.

1. Introduction

By analysing observations made from the Haute-Provence Observatory during 1950–51 Barbier *et al.* (1951) established that between the nightglow features in the green part of the spectrum there is a continuum. The only explanation for the phenomenon to have received more than passing attention is that the NO_2 air afterglow is responsible as Krassovsky (1951) proposed. Much laboratory research has been done on this striking afterglow which is due to the composite process

$$NO + O + M \longrightarrow NO_2 + M + h\nu \tag{1}$$

with the NO being regenerated by the fast reaction between NO_2 and O.

Beginning with the investigation by Nicolet (1949) on the origin of D-region ionization nitric oxide has been recognized as an important atmospheric constituent in the layer centred on the 98 km level from which rocket measurements (cf. Greer & Best 1967) have shown the green continuum emanates. Aeronomers have long appreciated that the NO_2 air afterglow must contribute to the nightglow and, in the apparent absence of any alternative, the presumption that it is the main source of the continuum is widely adopted as dogma. Indeed the intensity of the continuum is used as a means of gauging the value of the product [NO] [O] during the dark hours (cf. Donahue 1974). However, critical examination discloses that composite process (1) contributes only a fairly small fraction of the nightglow continuum in the visible region of the spectrum and only a minute fraction in the near infrared region and has other serious failings. It is easy to draw up a comprehensive list of like association processes that occur in the lower thermosphere and to establish that none even rivals the rejected NO_2 air afterglow. This will be done and a novel source will be proposed.

2. Air afterglow

Before proceeding some laboratory results on the NO_2 air afterglow will be summarized briefly for reference purposes.

Fontijn *et al.* (1961) have determined the spectral distribution of the emission to the short wavelength side of 14000 Å and shown that it is virtually independent of

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the total pressure in the range 0.1–5 Torr. They found that the continuum has a threshold at 3875 Å and that its intensity passes through a maximum at 6400 Å. Becker *et al.* (1972) have carried out extensive measurements on the afterglow at a fixed temperature, 296 K, and at pressures from 10^3 down to 0.25 mTorr which covers the pressure range relevant for the nightglow. As the pressure is reduced to low values the wavelength of the maximum drifts towards about 5600 Å and the fall-off on the long wavelength side of the maximum becomes considerably sharper. The collision processes in composite (1) are binary radiative association

$$\mathrm{NO}+\mathrm{O}\xrightarrow{k_2}\mathrm{NO}_2+h\nu \tag{2}$$

and termolecular association

$$\mathrm{NO}+\mathrm{O}+\mathrm{M}\xrightarrow{k_3}\mathrm{NO}_2^*+\mathrm{M} \tag{3}$$

in which NO_2^* is electronically and, in general, vibrationally excited and may experience collisional quenching

$$\mathrm{NO}_2^*+\mathrm{M}\xrightarrow{k_q}\mathrm{NO}_2+\mathrm{M} \tag{4}$$

or may radiate

$$\mathrm{NO}_2^*\xrightarrow{A}\mathrm{NO}_2+h\nu. \tag{5}$$

Becker *et al.* (1972) showed that the volume emission rate at wavelength λ may be represented by

$$V(\lambda)=[\mathrm{NO}]\,[\mathrm{O}]\,k_{\mathrm{eff}} \tag{6}$$

where k_{eff} is an effective rate coefficient given by

$$k_{\mathrm{eff}}=k_2\left\{1+\frac{(k_3/k_2)\,[\mathrm{M}]}{1+(k_q/A)\,[\mathrm{M}]}\right\}. \tag{7}$$

With the object of making the notation obvious we have arranged that the subscripts 2 and 3 both refer to the equation numbers and tell whether the process is binary or termolecular. Reminders that $k_2, k_3/k_2$ and k_q/A depend parametrically on λ have been omitted for compactness. The first term within braces on the right of the equation (7) is dominant when [M] is low and the second term is dominant when [M] is high. Published information (Becker *et al.* 1972) enables the values of $k_2, k_3/k_2$ and k_q/A at 296 K at any chosen wavelength to be found.

The spectral distribution cannot change with temperature in the low pressure limit where only binary association contributes. Measurements by Golomb & Brown (1973) have proved that it does not change appreciably between 217 and 363 K in the high pressure region. Hence if the high pressure temperature variation of the total association rate coefficient is represented by a function $F(T)$ which is adjusted to be unity at 296 K the generalization of equation (7) that allows for the effect of temperature is simply

$$k_{\mathrm{eff}}=k_2\left\{1+\frac{(k_3/k_2)\,[\mathrm{M}]\,F(T)}{1+(k_q/A)\,[\mathrm{M}]}\right\} \tag{8}$$

(McDade *et al.* 1986). A laboratory study by Whytock *et al.* (1976) yields

$$F(T)=\exp\{1.97\,(296-T)/T\}, \tag{9}$$

which corresponds to only a modest correction at the temperature (around 200 K) of the lower thermosphere.

3. Rocket investigations

The most revealing investigation of its type is that of McDade *et al.* (1986) in which two rockets were launched within a quarter of an hour period from South Uist, Scotland, on the night of 23 March, 1982, when $F(10.7\ \mathrm{cm})$ was 202 indicating considerable solar activity. Each of them had a forward-looking filter photometer, one of the filters being centred at 5400 Å, the other being centred at 7140 Å. The altitude profile of [O] was also measured. Using result (8) McDade *et al.* (1986) hence derived [NO] profiles getting good agreement with the results of a previous flight (McDade *et al.* 1982) made under quiet solar conditions with a 5320 Å filter photometer. Such profiles may be characterized by the peak number density $[\mathrm{NO}]_X$, the altitude z_X of this peak and the vertical distance Δz between the upper and lower levels at which the number density is half the peak. Table 1 compares the values of these characteristics with the corresponding values for a model [NO] profile that Frederick & Abrams (1982) judged appropriate to adopt as a reference in a study of nitric oxide fluorescence in the Earth's backscattered spectrum. It is based on a measured profile (Meira 1971) adjusted to take into account a change in the accepted (1, 0) gamma band oscillator strength. As Frederick & Abrams (1982) noted the true profile is variable in space and time and a profile that differs greatly from the model is not necessarily incorrect. Because of the high $[\mathrm{NO}]_X$ they derived, $2.5\times10^8\ \mathrm{cm}^{-3}$ at 104 km, McDade *et al.* (1982) had questioned whether the NO_2 air afterglow suffices for the green continuum. In the later paper (McDade *et al.* 1986) the variability of thermospheric nitric oxide was stressed and the view was taken that it may suffice but that it cannot generate all the radiation recorded by the 7140 Å photometer. McDade *et al.* (1986) speculated that the (4, 3) Atmospheric band of O_2 at 7154 Å may provide the shortfall but as will be seen in §4 ground level observations indicate near infrared continuum emission. Moreover a value of $[\mathrm{NO}]_X$ as high as the $3.1\times10^8\ \mathrm{cm}^{-3}$ inferred from their nightglow continuum measurements (table 1) cannot readily be reconciled with the data obtained from the ultraviolet spectrometer on the Solar Mesosphere Explorer satellite. Thus the highest daily average $[\mathrm{NO}]_X$ in the polar regions during the month of the launch is only $5\times10^7\ \mathrm{cm}^{-3}$ (Barth 1992); and the [NO] contour diagrams (Barth 1990) show that the peak is at about 110 km and that the thickness parameter Δz is always either as in the Meira model (table 1) or greater. The spectrometer data were acquired during the daylight hours. Stewart & Cravens (1978) have found that [NO] tends to decrease, by a factor of up to 2, between sunset and sunrise.

4. Ground level observations

Sternberg and Ingham (1982) carried out a seminal programme of observations on the night sky continuum over the 4100–8200 Å range from the Haute-Provence Observatory for a period of several years near sunspot maximum. Carefully subtracting out the contributions from starlight and from zodiacal light they found that the derived intensity of the nightglow continuum peaks at around 6000 Å, where it is $0.40R/A$, passes through a minimum and around 8200 Å averages $1.5R/A$. This structure and temperal variations found in the spectral distributions suggest more than one source. Both the high intensity in the infrared and the occurrence of variations have been confirmed. At Fritz Peak Observatory, Colorado, Noxon (1978)

Table 1. *Values of characteristics of* NO *profiles inferred from rocket measurements* (*McDade et al.* *1986*) *on the nightglow continuum*

	filter used		
characteristic	5400 A	7140 A	Meira model
$[NO]_X$ cm^{-3}	3.1×10^8	4.3×10^8	3.4×10^7
z_X km	104	100 and 106[a]	110
Δz km	$15\frac{1}{2}$	$18\frac{1}{2}$	27

[a] Two peaks.

found that the average continuum intensity near 8600 is $0.7R/A$ with a real variation between 0.6 and $1.2R/A$. At the Zvenigorod station in the Crimea Sobolev (1978) observing at 8210, 9268 and 10612 Å, where there are no hydroxyl lines found that the continuum intensity is $1\text{–}2R/A$ and that it does not rise markedly with increase in wavelength as had earlier been inferred through a misunderstanding, later elucidated by Noxon (1978), of the nightglow atlas of Broadfoot & Kendall (1968). The misunderstanding had led Gadsen & Marovich (1973) to invoke as the source the binary chemiluminescent process

$$NO + O_3 \longrightarrow NO_2 + O_2 \tag{10}$$

to which Dalgarno (1969) had drawn attention. However, the spectral distribution of this infrared chemiluminescence (Clough & Thrush 1967) is utterly disparate from that observed by Sobolev (1978) and, as may easily be verified, the contribution to the nightglow is inappreciable.

A juxtaposition was displayed by Sternberg & Ingham (1972) of the spectral distribution they obtained for the nightglow continuum with that of the NO_2 air afterglow as measured by Fontijn *et al.* (1964). The similarity between the two distributions was deemed to lend support to the thesis that they have a common origin. However, the juxtaposition is misleading in that the NO_2 air afterglow distribution used relates to high pressures. The distribution appropriate to the pressure of the atmospheric region concerned is needed for a meaningful comparison such as that in table 2 (which was prepared from the data of Becker *et al.* (1972)). As may be seen the NO_2 air afterglow distribution, normalized so that its peak in the green equals the corresponding nightglow peak, is significantly deficient in the red region and is drastically so in the infrared region. The red deficiency is in agreement with the rocket results of McDade *et al.* (1986).

Adopting the Meira model [NO] altitude profile referred to in §3 and taking the parameters in equation (8) to have the values that McDade *et al.* (1986) derived from the laboratory data we calculate that if the observed nightglow intensity at 5400 Å (table 2) is to be explained by composite process (1) then [NO] at 104 km would have to be as great as 2×10^8 cm^{-3}. Allowing for the difference between the Δz values (table 1) it may be seen that the rocket measurements and ground level observations agree quite satisfactorily. Sternberg & Ingham (1972) cite six earlier ground level determinations of the nightglow continuum in the green region of the spectrum. Like the intensity of the later determination of Gadsen & Marovich (1973) the intensities reported are around the same as the intensity they themselves obtained or are stronger. It is not credible that [NO] was abnormally high in all these cases.

Compelling evidence against process (1) being responsible for the nightglow continuum in the visible spectral region was adduced many years ago by Barbier &

Table 2. *Spectral distributions of continua*

wavelength/Å	absolute nightglow intensity[a] (R/A)	normalized air afterglow intensity (R/A)
4500	0.15	0.20
5000	0.23	0.33
5500	0.35	0.40
6000	0.40	0.38
6500	0.39	0.34
7000	0.38	0.27
7500	—	0.16
8000	—	0.12
8500	1.5[b]	0.08
9000	0.7[c]	0.05
9500	0.8[d]	0.03
10000	—	0.02
10500	—	0.01
11000	1.6[e]	—

[a] The first six entries are from Sternberg & Ingham (1972) and are at the wave lengths indicated. The remaining entries are as follows: [b] Sternberg & Ingham (1972) at 8200 Å and Sobolev (1978) at 8210 Å; [c] Noxon (1978) at 8600 Å; [d] Sobolev (1978) at 9268 Å; [e] Sobolev at 10612 Å.

Glaume (1960). It came from recordings of the nightglow intensity that were made at a low latitude station over a three year period around sunspot maximum. A photometer fitted with eight colour filters was used. Unique among such investigations the photometer was pointed in the poleward direction so as to minimize the variation of the intensity of the extraterrestrial light. Subtraction of the intensity of this light gave the nightglow intensities $I(\mathrm{OH})$, $I(\mathrm{Na})$, $I(6300)$, $I(5577)$, $I(\mathrm{O_2\,i})$, $I(\mathrm{O_2\,ii})$ and $I(\mathrm{cont.})$ where the spectral features concerned are indicated by the contents of the parenthesis OH signalling Meinel hydroxyl bands, Na signalling the sodium D doublet, 6300 and 5577 signalling the forbidden red and green lines of atomic oxygen, $\mathrm{O_2\,i}$ and $\mathrm{O_2\,ii}$ signalling mixes of bands of the Herzberg I, II, III and Chamberlain systems of molecular oxygen in broad regions around 4400 and 3670 Å and cont. signalling the continuum near 5260 Å. It was found that $I(\mathrm{cont.})$ does not correlate with $I(\mathrm{OH})$, $I(\mathrm{Na})$ or $I(6300)$ but correlates closely with $I(5577)$, $I(\mathrm{O_2\,i})$ and $I(\mathrm{O_2\,ii})$. Representative plots were published illustrating the convincingly precise covariance of $I(\mathrm{cont.})$, $I(5577)$, $I(\mathrm{O_2\,i})$ and $I(\mathrm{O_2\,ii})$ through each of three nights. In two of these the variations were complicated with the intensities passing through four maxima making the covariance truly remarkable. The correlation coefficients between $I(\mathrm{cont.})$ and $I(5577)$, $I(\mathrm{O_2\,i})$ and $I(\mathrm{O_2\,ii})$ averaged over these nights are as high as 0.970, 0.984 and 0.989 which are not significantly different from the correlation coefficient between $I(\mathrm{O_2\,i})$ and $I(\mathrm{O_2\,ii})$ which is 0.977. An analysis of all the results acquired revealed that the correlation coefficient between $I(\mathrm{cont.})$ and, for instance, $I(\mathrm{O_2\,i})$ is high (0.953) and further that

$$I(\mathrm{cont.}) \propto I(\mathrm{O_2\,i}). \tag{11}$$

This proportionality would be impossible if the continuum were generated by the $\mathrm{NO_2}$ air afterglow because $I(\mathrm{cont.})$ would then be governed by equation (6) whereas the oxygen bands are known to be generated by termolecular association and are strongly quenched by $\mathrm{O_2}$ or $\mathrm{N_2}$ (cf. Bates 1988, 1992) so that

$$I(\mathrm{O_2\,i}) \propto [\mathrm{O}]^2. \tag{12}$$

Aside from this disagreement the high correlation coefficients quoted would be inconsistent with fluorescent measurements made from the Solar Mesosphere Explorer satellite. These show that even at low latitudes the abundance of nitric oxide changes rapidly and irregularly by factors in excess of 2 near sunspot maximum and that it changes by a factor of around 10 over a three year period (Barth 1992).

The principal objections to the theory that the nightglow continuum is produced by composite process (1) are the high $[\mathrm{NO}]_X$ required, relation (11) and the correlations. Although minor by comparison the Δz discrepancy (table 1) is quite telling. These objections are sufficient to render the theory untenable. Furthermore it may be seen from table 2 that, in the near infrared region, there is no accord at all with nightglow measurements made at three stations.

5. Source

Since the source of the nightglow continuum that will be proposed is novel and supporting laboratory evidence is not available we will first demonstrate that a novel source is necessary by systematically listing and quickly eliminating all conceivable stock sources.

Because of the rarity of charged species it is clear that the continuum must arise from the association of neutral atoms and molecules. Without the involvement of free O atoms, which are the major energy bearers in the lower thermosphere, the intensity would obviously be far too low. Consideration of the constituents of the lower thermosphere (cf. Rodrigo *et al.* 1986) shows that the only collision partners that need to be considered are the other O atoms, N, H, O_2 and CO.

Dalgarno *et al.* (1992) have made preliminary estimates of the rate coefficient for

$$\{\mathrm{O}+\mathrm{O}\}\,1^3\Pi_u \longrightarrow \mathrm{O}_2(\mathrm{X}^3\Sigma_g^-)+h\nu. \tag{13}$$

They reckoned that at 300 K and 1000 K it is of order 10^{-23} cm^3 s^{-1} and 10^{-21} cm^3 s^{-1} respectively and that the total emission from the thermosphere approaches 1×10^3R. However, owing to the repulsive $1^3\Pi_u$ potential most of emission is, as they noted, in the far infrared beyond 5 μm. This makes process (13) of no interest in the present context.

Radiative association of O with N

$$\{\mathrm{O}+\mathrm{N}\}\,\mathrm{I}^2\Sigma^+ \longrightarrow \mathrm{NO}(\mathrm{X}^2\Pi)+h\nu \tag{14}$$

entails approach along a repulsive potential (Michels 1981) and therefore far infrared emission. It is much slower than association by inverse pre-dissociation followed by a band emission. Rocket measurements by McCoy (1983) have shown that the volume emission rate of the strongest of the bands, the (0, 1) delta band, peaks at an altitude of 160 km (which is considerably above the luminous layer) and corresponds to an intensity less than about $10R$ (which is only some 1 % of even the limited part of the integrated intensity of the nightglow continuum up to 7000 Å). The band emission is in the ultra violet its maximum being at 209.5 nm (Du & Dalgarno 1990).

In the case of

$$\{\mathrm{O}+\mathrm{H}\}^2\Sigma^- \longrightarrow \mathrm{OH}(\mathrm{X}^2\Pi)+h\nu \tag{15}$$

the initial potential (Michels & Harris 1969; van Dishoeck *et al.* 1983) is again repulsive and the emission is in the far infrared region of the spectrum. The dominant binary association process is by inverse pre-dissociation to the $A^2\Sigma$ state (Smith *et al.* 1974). It leads to the emission of bands in the near ultra violet (Smith 1970). These have not been identified in the standard nightglow atlas of Broadfoot & Kendall (1968) although a neighbouring band of the Herzberg I system estimated by Degen (1977) to have an intensity of about $25R$ is prominent.

Taking into account the results of *ab initio* computations by Banichevich *et al.* (1990) on O_3 Dalgarno *et al.* (1990) have considered

$$(O+O_2)\,C^1A'' \longrightarrow O_3(X^1A')+h\nu \tag{16}$$

concluding that the rate coefficient at 300 K is unlikely to exceed 10^{-23} cm^3 s^{-1} from which we calculate that the photon emission rate is unlikely to exceed about $30R$. Inspection of the *ab initio* potential energy curves given by Banichevich *et al.* (1990) shows that only a very minute fraction of the emission in the spectral region of the observed continuum is to the short wavelength side of 1.1 μm. In composite termolecular association

$$O+O_2+M \longrightarrow O_3+M+h\nu \tag{17}$$

there may be emission from O_3 in the metastable $^3B_2$ state but it is expected at 3.3 μm with safe uncertainty bounds of 2.1 and 6.9 μm (van Rosenberg *et al.* 1975).

Binary radiative association of CO with O is spin forbidden and may therefore be ignored. A laboratory study of the blue chemiluminescence process

$$CO+O+M \longrightarrow CO_2+M+h\nu \tag{18}$$

by Clyne & Thrush (1962) has shown that it has an activation energy of (3.7 ± 0.5) kcal mol^{-1} and that its rate coefficient is less than 2×10^{-3} of that of process (1) at 293 K so that taking $F(T)$ of equation (9) into account it is less than 1×10^{-4} of that of process (1) at 200 K. Now [CO] in the 90–100 km region (cf. Rodrigo *et al.* 1986) is only about 10 times the value that [NO] would have to be for process (1) to explain the observed continuum near 5300 Å. It is hence evident that process (18) does not make an appreciable contribution.

No other constituent of the lower thermosphere is sufficiently abundant to merit discussion.

The sole remaining possibility is that a continuum is emitted in the composite process

$$O+O+M \longrightarrow O_2+M+h\nu. \tag{19}$$

Moreover relation (11) and the singular correlation discovered by Barbier & Glaume (1969) between I(cont.) and $I(O_2\,\mathrm{i})$, $I(O_2\,\mathrm{ii})$ and $I(5577)$ point unambiguously to this process (at least for the portion in the visible region) since it is the source of the Herzberg, I, II and III and Chamberlain band systems, and also after an energy transfer collision, the forbidden green line (cf. Bates 1992).

A search has revealed only one way by which termolecular association might yield a continuum of the required intensity.

Let $O_2(\neq)$ denote an oxygen molecule in one of the six metastable states ($a^1\Delta_g$, $b^1\Sigma_g^+$, $c^1\Sigma_u^-$, $A'^3\Delta_u$, $A^3\Sigma_u^-$ and $^5\Pi_g$) that are populated by termolecular association. We propose that a collision between $O_2(\neq)$ and another molecule or atom is intimate enough to form a complex that dissociates radiatively by an allowed transition. Inspection of the potential energy curves of diatomic molecules shows that conditions for an allowed transition are, in many instances, created when a metastable and normal atom approach. This must also be true of molecules with the vital difference that the duration of the intimate collision may be much longer because of the high energy density of the rovibrational levels of the complex. In general the radiative transition ensures the dissociation of the complex so that the emission forms a continuum.

For the sake of definiteness suppose that the collision partner is a normal oxygen molecule. The proposed sequence is then

$$O_2(\neq) + O_2(X^3\Sigma_g) \rightleftharpoons O_4(*), \tag{20}$$

$$O_4(*) \longrightarrow O_2' + O_2'' + h\nu, \tag{21}$$

the primes being reminders that the products are not necessarily in the ground electronic state.

Using rocket data (Greer *et al.* 1986) we find that if the collision partner is $O_2(X^3\Sigma_g^-)$ or $N_2(X^1\Sigma_g^+)$ the emission would peak near 96 km and that the thickness of the luminous layer (defined as the vertical distance between the levels where the intensity is half the maximum) would be 10 km. These values are in satisfactory agreement with the rocket measurements of McDade *et al.* (1986).

The volume emission of the continuum due to the displayed sequence (20) and (21) is

$$V(\text{cont.}) \equiv Z[O_2(\neq)]\,[(O_2)\,X^3\Sigma_g^-]\,r(*), \tag{22}$$

where Z is the rate coefficient (say 1×10^{-10} cm^3 s^{-1}) for collisions on a surface with a well and

$$r(*) = A(R)/k(D), \tag{23}$$

$A(R)$ and $k(D)$ being the respective rate at which $O_4(*)$ dissociates by photon emission and by the inverse of the process by which it was formed. Clearly $r(*)$ must be such as to satisfy the unequality

$$Zr(*) < k_q, \tag{24}$$

k_q being the $O_2(\neq)$-$O_2(X^3\Sigma_g^-)$ quenching coefficient. To account for the nightglow the maximum volume emission $V_X(\text{cont.})$ must be around 1×10^3 cm^3 s^{-1} in the visible region and around 5×10^3 cm^3 s^{-1} in the near infrared region (cf. table 2).

Several of the combinations may be immediately dismissed. Although $[O_2(b^1\Sigma_g^+)]$ is as high as 5×10^4 cm^{-3} near 95 km (cf. Bates 1988) where $[O_2(X^3\Sigma_g^-)]$ is about 7×10^{12} cm^{-3} the combination contributes little. Thus the quenching of $O_2(b^1\Sigma_g^+)$ by $O_2(X^3\Sigma_g^-)$ is exceptionally slow with k_q only 5.6×10^{-17} cm^3 s^{-1} (Knickelbein *et al.* 1987) so that inequality (24) limits $V_X(\text{cont.})$ to 20 cm^3 s^{-1}. Its quenching by the more abundant $N_2(X^1\Sigma_g^+)$ is less slow with k_q about 2×10^{-15} cm^3 s^{-1} (Martin *et al.* 1976) but emission in the spectral range of interest requires a spin-change transition and hence may be disregarded. A spin-change transition is also required for emission by $O_2(^5\Pi_g) \cdot N_2(X^1\Sigma_g^+)$ and finally $O_2(a^1\Delta_g)$ partnered by a ground state molecule does not have enough energy.

The remaining combinations are

$$(*,1) \equiv O_2(^5\Pi_g) \cdot O_2(X^3\Sigma_g^-) \quad \{2.0 \times 10^{-3}\}, \tag{25}$$

$$(*,2) \equiv O_2(\text{trio}) \cdot O_2(X^3\Sigma_g^-) \quad \{1.0 \times 10^{-2}\}, \tag{26}$$

$$(*,3) \equiv O_2(\text{trio}) \cdot N_2(X^1\Sigma_g^-) \quad \{2.5 \times 10^{-3}\}, \tag{27}$$

where $O_2(\text{trio})$ denotes the close metastable trio, $O_2(c^1\Sigma_v^-, A'^3\Delta_u$ and $A^3\Sigma_u^+)$ taken together

$$(*,4) \equiv O_2(a^1\Delta_g) \cdot O_2(a^1\Delta_g) \quad \{4.0 \times 10^{-4}\}. \tag{28}$$

Table 3. *Radiative transition rates $A(R)\,(s^{-1})$ required for nightglow continuum*
((∗1), (∗2) and (∗3) visible; (∗4) near infrared.)

assumed association energy E_0/eV	∗1	∗2	∗3	∗4
0.25	5×10^{7}	5×10^{8}	1×10^{8}	4×10^{7}
0.50	5×10^{6}	6×10^{7}	2×10^{7}	6×10^{6}
1.00	3×10^{5}	4×10^{6}	1×10^{6}	5×10^{5}
1.50	6×10^{4}	7×10^{5}	2×10^{5}	1×10^{5}

Energy considerations indicate that the emissions arising from (∗, 1), (∗, 2) and (∗, 3) are in the visible region while that from (∗, 4) is in the near infrared region. Independent intensity variations in the two regions (§4) would be possible since some of the $O_2(a^1\Delta_g)$ is generated from hydroxyl (cf. Llewellyn & Solheim 1978).

Direct information on $[O_2(^5\Pi_g)]$ is not available. For illustrative purposes it will be taken to be a quarter the 200 K steady-state value (Bates 1992) pertaining to

$$O+O+M \rightleftharpoons O_2(^5\Pi_g)+M. \tag{29}$$

The number densities in the other metastable states are known (Llewellyn & Solheim 1978; Bates 1988, 1992) from nightglow studies. Hence the value of $r(*)$ of equation (18) needed to $V(\mathrm{cont})_X$ may be calculated. They are given in braces on the right of the chemical representation of the complex. Each of the first three values was calculated on the assumption that the other two are zero.

The radiative transition probabilities $A(R)$ must be rather low, perhaps around 10^6–10^7 s^{-1} for emission in the visible region and 10^5–10^6 s^{-1} for emission in the near infrared region. Using crude estimates of the frequencies of the normal vibrational modes of the electronically excited complexes the dissociation rates $k(D)$ were computed as a function of the association energy E_0 from a standard formula (Tröe 1977) of unimolecular theory. In conjunction with $r(\neq)$ they enable the values of $A(R)$ needed to account for the nightglow continuum (visible and near infrared) to be obtained. Table 3 gives these values. Because of the unavoidable uncertainties the limited objective in giving them is to show that it is plausible to suppose that the novel continuum source proposed is strong enough. This is a necessary supplement to the argument rooted in the absence of any viable alternative and the positive evidence provided by relation (11) and the correlations (Barbier & Glaume 1960). A laboratory check is needed. Note in this connection that the rate coefficient relating to the emission of the visible continuum of process (19) is only around 2×10^{-34} cm^6 s^{-1} which is much less than the corresponding rate coefficient, 7×10^{-32} cm^6 s^{-1}, for the continuum of process (1) (Becker *et al.* 1972).

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