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Phil. Trans. R. Soc. Lond. A 1969 264, 153-160

doi: 10.1098/rsta.1969.0009

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Infrared day and night airglow of the Earth's upper atmosphere

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A list is presented of the principal emission features of the airglow spectrum in the infrared and the expected intensities and altitude distributions are discussed.

1. Introduction

The day and night airglow emission of the atmosphere in the infrared region of the spectrum may be a serious hindrance to infrared astronomy but it can provide valuable information on the energy content of the atmosphere and of the reactions that take place.

Most of the infrared emission of the Earth's atmosphere arises from minor constituents, of which the most important are H₂O and CO₂ and their isotopes. Also produced at the surface of the Earth are the infrared active constituents CH₄, N₂O, CO and NO₂. At high altitudes, the action of solar radiation gives rise to O₃, H₂O₂, HO₂, OH, NO, CO and NO⁺.

2. Thermal emission features

2.1. Water vapour

The infrared spectrum of H₂O is complex. There are three fundamental rotationvibration bands ν_1 , ν_2 , and ν_3 occurring at 2.74, 6.25 and 2.66 μ m respectively of which the ν_2 band is the strongest. The $2\nu_2$ band lies at $3.17 \,\mu\mathrm{m}$ and together with the ν_1 and ν_3 bands and some weak bands of CO₂ constitutes the strong X-band in the solar spectrum (cf. Goody 1964). The pure rotation spectrum occupies the entire infrared region with the strongest lines appearing near 50 µm. Detailed calculations of infrared absorption by H₂O have been reported by Zhevakin & Naumov (1963) and Bastin (1966). Fundamental emissivity studies have been carried out by Edwards, Flornes, Glassen & Sun (1965), by Ludwig, Ferriso & Abeyta (1965) and by Penner & Varanasi (1965).

Goody (1964) has shown that up to altitudes of about 75 km, thermodynamic equilibrium prevails for the rotation-vibration spectrum of H₂O and various calculations using Kirchhoff's law of the cooling rates associated with the infrared emission of H₂O have been reported, the most recent of which is that by Rodgers & Walshaw (1966).

The water-vapour content of the low atmosphere is very variable, and Rodgers & Walshaw (1966) carried out calculations for a number of different humidity ratios. The variation with altitude of the humidity ratio is a parameter of considerable importance, about which conflicting views have been expressed. However, recent measurements of the intensity of emission of the 6.25 µm H₂O band with a balloon-borne radiometer (Williamson & Houghton 1965) showed that the water-vapour mixing ratio decreased rapidly to a value of $(2-3) \times 10^{-6}$ at the tropopause and remained approximately constant at

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 $(2-3) \times 10^{-6}$ in the stratosphere up to 24 km and balloon observations of the altitude variation of the infrared solar absorption near 2.6 µm suggest that the mixing ratio typically increases again above 24 km and approaches values of between 10^{-5} and 10^{-4} above 30 km (Murcray, Murcray & Williams 1966). Expressed as a percentage of that received from a blackbody at the local air temperature (200 to 220 °K), the emitted intensity observed by Williamson & Houghton decreased from 15% at an altitude of 12 km to 4 % at 30 km. The origin of the 4 % signal from above 30 km has not been identified. The 6.3 µm band of H2O has also been observed in the nightglow above 30 km by Hampson (cf. Houghton 1965).

Because of the dissociating action of solar radiation, the fractional abundance of water vapour must decrease with increasing altitude above about 60 km. The most recent calculation of the altitude distribution is that of Hunt (1966). It is based upon photochemical equilibrium considerations and ignores mixing effects except that the total content of hydrogen compounds is specified by the water-vapour mixing ratio which is taken to be independent of altitude.

2.2. Carbon dioxide

The fundamental rotation-vibration bands of CO_2 occur near 15 and $4\cdot3\,\mu\text{m}$. Other less strong bands of CO₂ occur between 1.4 and 15 µm and calculations of their intensity have been summarized by Goody (1964) (see also Rasool 1964).

Thermodynamic equilibrium prevails for the rotation-vibration spectrum up to about 75 km (Goody 1964) and Rodgers & Walshaw (1966) have calculated the altitude profile of the cooling rates associated with the infrared emission of the 15 µm bands. Radiative cooling above 30 km is dominated by the emission in the 15 μ m bands and it plays an important role in determining the location of the mesopause near 80 km.

The fractional volume abundance of CO_2 at ground level is about 3×10^{-4} and its total abundance in the atmosphere is about 10²² molecules/cm² column. It is not chemically reactive and probably remains uniformly mixed throughout the stratosphere and mesosphere (cf. Bates & Witherspoon 1952; Goody 1964). Carbon dioxide can be dissociated by solar ultraviolet radiation into carbon monoxide and atomic oxygen and its fractional abundance will decrease rapidly above 100 km. Metastable O¹D atoms may be important in reforming CO₂ after its dissociation.

The 4·3 µm band has been observed in emission in the nightglow above 30 km by Hampson (cf. Houghton 1965) with a peak intensity of $2 \mu W \text{ cm}^{-2} \text{ sr}^{-1} \mu \text{m}^{-1}$.

2.3. *Ozone*

The infrared spectrum of O_3 has strong bands at 14·1, 9·6 and 4·75 μm and weaker bands at 5.8, 3.6 and 3.3 µm (cf. Goody 1964). The cooling rates associated with the emission of the 9.6 µm band have been estimated by Rodgers & Walshaw (1966) and it has been detected at the ground (Murcray 1961; Dave, Sheppard & Walshaw 1963).

Ozone is produced by the dissociation of molecular oxygen and the recombination of atomic and molecular oxygen. Photochemical equilibrium calculations (Hunt 1966) yield an altitude profile with the maximum concentration occurring at 30 km and a total abundance of 5×10^{18} molecules/cm² column. The actual ozone abundance in the

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troposphere and lower stratosphere varies with season and latitude, but probably remains fairly constant at higher altitudes except for a day-night variation about 80 km. Recent experimental altitude profiles have been reported by Miller & Stewart (1965), by Randhawa (1966) and by Carver, Horton & Burger (1966).

2.4. Nitrous oxide

The three fundamental rotation-vibration bands of N₂O are located at 7·8, 17·0 and $4.5 \,\mu\text{m}$. Goody (1964) has given a list of other weaker bands between 2 and 17 μm and the pure rotation spectrum between 100 and 600 µm has been measured by Palik & Rao (1956).

Nitrous oxide has been detected in absorption and the total abundance in the atmosphere is about 1×10^{19} molecules/cm² column. The fractional abundance in the troposphere is about 2.5×10^{-7} .

The altitude distribution and photochemistry of N₂O have been discussed by Bates & Witherspoon (1952) and by Bates & Hays (1967). Because of the finite vertical exchange coefficient, the fractional abundance must decrease with altitude in the stratosphere.

2.5. Methane

Methane has strong rotation-vibration bands at 3.3 and $3.85 \,\mu\mathrm{m}$. These bands and others between 1.7 and 7.7 μ m have been observed in the solar spectrum (cf. Goody 1964). Methane has no pure rotation spectrum.

Its total abundance in the atmosphere is about 3×10^{19} molecules/cm² column and the fractional volume abundance in the troposphere is about 2×10^{-6} . It is destroyed by atomic oxygen and its fractional abundance decreases rapidly in the stratosphere. It is an important source of water vapour in the stratosphere (Bates & Nicolet 1965).

2.6. Carbon monoxide

The fundamental rotation-vibration band of CO lies at $4.7 \mu m$ and its first overtone at $2.4 \,\mu\mathrm{m}$. The rotation spectrum between 100 and 600 $\mu\mathrm{m}$ has been studied in the laboratory by Palik & Rao (1956).

Its total atmospheric abundance is variable around an average value of about 2×10^{18} molecules/cm² column. In the troposphere its fractional volume abundance is about 7×10^{-8} . The altitude profile is unknown, but CO probably remains mixed up to altitudes in the region of 90 km when it is affected by the photodissociation of carbon dioxide.

An emission feature near $4.8 \,\mu m$ has been seen in the night airglow above 30 km by Hampson (cf. Houghton 1965), who explored the spectral range from 4 to 8 μ m. The observed intensity was of the order of $1 \mu W \text{ cm}^{-2} \text{ sr}^{-1} \mu \text{m}^{-1}$. It has been tentatively ascribed to NO⁺ but CO provides a more plausible explanation.

2.7. Nitrogen dioxide and nitric oxide

The fractional abundance of NO_2 and NO at ground level is about 3×10^{-9} . Neither constituent has been detected in absorption. An upper limit of 5×10^{16} molecules/cm² column has been placed on the daytime abundance of NO (Migeotte & Neven 1952). The

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fundamental rotation-vibration band of NO lies at 5·32 μm (for recent laboratory work see Ford & Shaw 1965) and occurs in a region of strong water-vapour absorption. The intensities of individual lines of the band have been calculated by Carpenter & Franzosa (1965). The pure rotation spectrum between 100 and 600 μ m has been studied by Palik & Rao (1956).

The altitude profiles of NO and NO₂ are affected by the presence of a strong source of odd nitrogen atoms in the ionosphere (cf. Nicolet 1965) and it appears that the fractional volume abundance will increase with increasing altitude through the mesosphere. The total abundance must be close to the upper limit derived by Migeotte & Neven (1952).

The midday abundance of NO at altitudes between 76 and 125 km has been determined by Barth (1966) from an analysis of the dayglow emission of the γ-band system which assumes the emission arises from fluorescent scattering of solar radiation. The number density of NO decreased from 6.2×10^7 cm⁻³ at 76 km to 6.0×10^7 cm⁻³ at 90 km to 6.0×10^6 cm⁻³ at 125 km and the column density above 76 km was 2.5×10^{14} cm⁻². The concentration measured at 76 km corresponds to a mixing ratio of 10⁻⁷, substantially larger than that obtaining in the troposphere.

The mean time for the excitation of the first vibrational level of NO is about $10^{16}/n(M)$ second (cf. Dalgarno 1963) where n(M) is the total number density and the radiative lifetime is about 10⁻¹ s (Penner & Weber 1952; Breene 1958). Thermal equilibrium should prevail at altitudes up to about 75 km and the thermal emission flux below 75 km is accordingly of the order of 1 erg cm⁻² s⁻¹ or 3 MR (megarayleighs). It will be absorbed by water vapour in the lower atmosphere.

2.8. Hydrogen peroxide

HO₂ is produced in the atmosphere by a sequence of reactions initiated by the photodissociation of water vapour (Bates & Nicholet 1950). The total abundance predicted by photochemical equilibrium theory is 2×10^{14} molecules/cm² column and the maximum concentration occurs at 35 km (Hunt 1966). Its infrared spectrum is unknown. H₂O₂ is also produced in the atmosphere. The total abundance predicted for H_2O_2 is 10^{16} molecules/cm² column and its maximum concentration occurs at 30 km (Hunt 1966). These figures are subject to large uncertainties.

The infrared spectrum of H₂O₂ has been analysed by Hunt et al. (1965).

2.9. Nitrogen and oxygen

Nitrogen and oxygen do not possess a permanent dipole moment but at low altitudes weak pressure induced emission can occur in the rotation spectrum. The maximum intensity is at $4.3 \,\mu\mathrm{m}$ for N_2 and at $6.4 \,\mu\mathrm{m}$ for O_2 . The pressure-induced absorption by N₂ and O₂ in the atmosphere has been calculated by Bastin (1966). It is usually negligible compared to that by H₂O and CO₂.

2.10. Atomic oxygen

Bates (1951) drew attention to the important role of transitions between the different levels of the ground term of atomic oxygen in the thermal budget of the upper atmosphere. The emission appears at 63 and 147 μ m and remains thermal throughout the atmosphere.

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Atomic oxygen is produced by the photodissociation of O_2 and of O_3 , but its distribution with altitude is greatly modified by transport processes. It attains a peak density exceeding 10¹¹ cm⁻³ at an altitude of 95 km. At night, it disappears below 70 km. The calculation of the altitude profile of the intensities is complicated and the actual atomic oxygen distribution is uncertain. The intensity of the nocturnal emission observed from below 80 km should be comparable to that from a blackbody at a temperature between 260 and 300 °K. There should occur an enhancement of the $63 \,\mu\mathrm{m}$ line during the day of about 0.1 erg cm⁻² s⁻¹ from the region between 30 and 80 km, if the photochemical predictions (Hunt 1966) of the daytime atomic oxygen concentrations are correct.

3. Non-thermal emission features

3.1. Hydroxyl

The rotation-vibration band system of OH produced by the reaction

$$O_3 + H \rightarrow OH^+ + O_2$$

is the most intense source of nocturnal infrared emission in the upper atmosphere (cf. Gush 1968, this volume, p. 161). The total intensity is about 4 MR (cf. Wallace 1962). It reaches its maximum in the region of 70 km or possibly somewhat higher. The OH emission has also been observed in the dayglow between 2·6 and 3·4μm (Lytle & Hampson 1964).

3.2. Infrared atmospheric system of oxygen

The infrared atmospheric system of molecular oxygen at 1.58 and 1.27 µm has been observed in the twilight, the dayglow and during a solar eclipse.† The daytime intensity of the $1.27 \,\mu\mathrm{m}$ band is about 10 MR and of the $1.58 \,\mu\mathrm{m}$ bands about 0.1 MR. The peak emission occurs at an altitude of 50 km (Llewellyn et al. 1967). The most efficient source of O_2 $(a^1 \Delta_{\rho})$ molecules is

$$O_3 + h\nu \rightarrow O + O_2 (a^1 \Delta_g)$$
.

3.3. The rotation-vibration band of NO⁺

The positive ion NO⁺ of nitric oxide is the principal ion in a substantial region of the ionosphere. The column content of NO⁺ during the daytime at solar minimum is about 5×10^{12} cm⁻² (cf. Johnson 1966). Collision processes will not be rapid enough to maintain a thermal population of vibrationally excited molecules. An upper limit to its daytime intensity can be obtained by assuming that NO+ is produced in a vibrationally excited state by the reaction $O^{+} + N_{2} \rightarrow NO^{+} + N$.

The resulting value is less than 10 kR (kilorayleighs) and it is unlikely that the feature near 4.8 µm observed by Hampson (cf. Houghton 1965) can be attributed to NO⁺.

† The $1.27 \,\mu\mathrm{m}$ emission explains the infrared dayglow brightness measurements of Gopshtein & Kushpil (1965) and possibly also the anomalous brightness of the post-twilight sky observed by Wolstencroft, Brandt & Rose (1966).

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3.4. The Meinel bands of N_2^+

The infrared Meinel bands of N₂⁺ are a strong emission feature of auroras. For an aurora of IBC III, the intensity is about 2500 kR, an order of magnitude larger than that of the blue-violet first negative system (cf. Chamberlain 1961). The infrared bands will also appear as a strong feature in the dayglow. Dalgarno & McElroy (1963, 1965) and Tohmatsu, Ogawa & Tsuruta (1965) have estimated intensities of about 10 kR from the photoionization of N₂ by solar ultraviolet radiation and Dalgarno & McElroy (1965) have suggested that there may occur an additional contribution of up to 4 kR from the charge transfer process

 $O^+(^2D) + N_2 \rightarrow O(^3P) + N_2^+ (a^2\Pi_u, v = 1, 0).$

Dalgarno & McElroy (1966) have later argued that the twilight observations of 3914 Å emission (Broadfoot & Hunten 1966) demand an additional source of N₂⁺ ions high in the atmosphere and they suggest that the source is charge-transfer from metastable $O^+(^2D)$ ions. The contribution to the intensity of the Meinel band system from resonance and fluorescent scattering by N₂⁺ ions has not been calculated but it may well be the main source. The 0–0 band lies at $1\cdot10\,\mu\text{m}$.

At night, the intensity may be of the order of 100 R.

3.5. The first positive system of N₂

The $B^3\Pi_g$ state of N_2 is populated during the day by impact excitation of fast photoelectrons produced by absorption of solar ultraviolet radiation in ionizing transitions and by cascading from the $C^{3}\Pi_{u}$ state through emission of the second positive system, the $C^{3}\Pi_{u}$ being populated by the impact of fast photoelectrons. There occurs also a smaller contribution from fluorescent scattering of solar radiation by the metastable $A^3 \Sigma_u^+$ state. The daytime intensity above 120 km may exceed 10 kR, most of which will appear in the 0-0, 1-0 and 2-0 bands at 1.04, 0.88 and 0.77 μ m respectively (Dalgarno, McElroy & Stewart 1968).

At night, the intensity probably does not exceed 100 R.

3.6. The atmospheric system of O_2

The 0–1 band at $0.86\,\mu\mathrm{m}$ of the atmospheric system of O_2 is a familiar feature of the night glow spectrum. The $b^{-1}\Sigma_{g}$ state is presumably populated by association of two oxygen atoms in a three-body collision. During the daytime, significant enhancement will occur through electron impact excitation and probably also through dissociation of ozone in the Hartley continuum

$$O_3 + h\nu \rightarrow O + O_2 \ (b \ ^1\Sigma_g, \ a \ ^1\varDelta_g)$$
 (Bates & Dalgarno 1954).

Because of uncertainties attending the efficiency of deactivation, it is difficult to make an accurate estimate of the daytime intensity of the atmospheric system but it is likely to be several kilorayleighs (excluding the 0-0 band which is absorbed by the lower atmosphere).

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The infrared lines of atomic oxygen

The infrared lines of atomic oxygen at 0.84 and $0.78 \mu m$, arising respectively from the transitions $3^3S^0-3^3P$ and $3^5S^0-3^5P$, appear quite strongly in aurora and they will also appear in the dayglow. The only excitation mechanism of importance is electron impact and the expected daytime intensities are of the order of 1 kR (Dalgarno, McElroy & Stewart 1968).

There is a chance coincidence between the wavelengths of Lyman beta and of the $2p^4$ ^3P-2p 33d 3D transition in atomic oxygen. The 2p 33d 3D state gives rise to radiation at $1.13 \,\mu\text{m}$. The absorption of Lyman β in the atmosphere has been investigated by Shlovskii (1957) and by Brandt (1959) and it appears that less than 100 R of $1.13 \,\mu m$ radiation will arise from the fluorescence of Lyman β .

3.8. Infrared lines of atomic nitrogen

The $2p^3 {}^2D^0 - 2p^3 {}^2P^0$ multiplet of atomic nitrogen appears at $1.04 \,\mu\mathrm{m}$. The ${}^2P^0$ state can be populated by electron impact of N_2 and by dissociative recombination of N_2^+

$$N_2^+ + e \to N(^4S) + N(^2P)$$
.

The daytime intensity is unlikely to exceed a few hundred rayleighs and the line will be difficult to detect since it lies in the region of the 0-0 band of the first positive system of N₂.

There are other lines of atomic nitrogen between 0.8 and $0.9 \,\mu m$ which have been detected during auroras. They will also be present in the dayglow but with a total intensity not exceeding 1 kR.

3.9. Infrared line of helium

The infrared line of helium at $1.08 \,\mu m$ has been detected during twilight and during sunlit auroras by Russian observers. The radiation is produced by resonance scattering of sunlight by metastable 2^3S helium atoms (Shefov 1961), the main source of $He(2^3S)$ atoms being impact by fast electrons (Shefov 1962; McElroy 1965). The twilight intensity is about 1 kR. McElroy (1965) has discussed the dayglow emission and his calculations show that the intensity may be somewhat less during the day.

3.10. Infrared emission of NO₂

The reaction

$$\mathrm{NO} + \mathrm{O_3} \rightarrow \mathrm{NO_2} + \mathrm{O_2}$$

is chemiluminescent and the luminosity occurs most strongly in the region of $1 \mu m$ (Greaves & Garvin 1959). The emission can probably be attributed to an excited state of NO₂. The intensity may be of the order of 10 MR, peaking near the ozone maximum.

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