

NITRIC OXIDE COOLING IN THE TERRESTRIAL THERMOSPHERE

G. Kockarts
 Institut d'Aéronomie Spatiale
 3 Avenue Circulaire
 B-1180 Bruxelles, Belgium

Abstract. A simple formulation of the nitric oxide cooling by the emission of the 5.3 μm fundamental band in the terrestrial thermosphere indicates that this process is an important mechanism which has been omitted previously in all thermospheric models. The cooling effect is highly variable as a consequence of its strong temperature dependence and of the observed variability of the nitric oxide concentration. The infrared emission is never in local thermodynamic equilibrium above 120 km altitude and the predominant cooling probably occurs during NO auroral enhancements.

Introduction

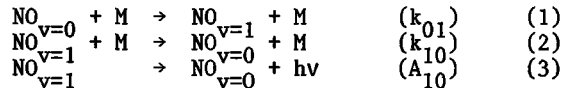
Although many physical mechanisms involved in the energy balance of the terrestrial thermosphere have been identified, there is still a significant uncertainty in their quantitative evaluation. This is particularly true for time variations of the solar extreme ultraviolet heating and for time and space variations of energy inputs such as Joule heating, particle precipitation and gravity waves dissipation. Less attention has been paid to possible energy loss mechanisms by infrared radiation. The possibility of an infrared loss at 63 μm due to the transition $\text{O}(^3\text{P}_1) \rightarrow \text{O}(^3\text{P}_2)$ was first demonstrated by Bates (1951). Such a mechanism is, however, not very efficient, since below 150 km the thermosphere becomes optically thick at 63 μm and a radiative transfer calculation (Kockarts and Peetermans, 1970) has shown that the volume emission rate decreases below 150 km compared to the optically thin case and becomes negligible around 100 km altitude. Furthermore, measurements by Grossmann and Offermann (1978) suggest that the 63 μm line of atomic oxygen is not in local thermodynamic equilibrium. As a consequence a further reduction of the infrared cooling occurs above 120 km altitude. In absence of any efficient loss mechanism very large temperature gradients would be permanently present around 120 km (Banks and Kockarts, 1973; Kockarts, 1975), and theoretical thermospheric models would lead to thermopause temperatures much higher than usually observed.

Satellite observations of molecular radiation of the upper atmosphere (Markov, 1969) indicated a maximum intensity in the 4.5 - 8.5 μm region more than ten years ago, and it was established by Gordiets and Markov (1977) that the infrared radiation above 120 km resulting from the 5.3 μm band of nitric oxide should play a role in the thermosphere heat balance. Strong enhancements of the 5.3 μm band have been observed by Stair et al. (1975) during high auroral activity. In a detailed analysis of infrared excitation processes, Ogawa (1976) has shown that

collisional excitation to the vibrational level $v = 1$ of the ground state $X^2\Pi$ of nitric oxide becomes more important than resonant absorption of solar and terrestrial radiation above 120 km altitude.

Nitric Oxide Cooling Rate

Since a search for an efficient cooling process is the present objective, only excitation mechanisms which extract kinetic energy from the atmosphere will be considered. The major collisional excitation mechanisms are vibrational exchange with other molecules and a process of oxygen atom exchange between nitric oxide and atomic oxygen as suggested by Dalgarno (1963). Considering excitation and deactivation of NO by collisions with an atmospheric constituent M and spontaneous emission, the population of the $v = 1$ level is determined by the following processes



where a photon with energy $h\nu = 1876 \text{ cm}^{-1} = 3.726 \times 10^{-13} \text{ erg}$ is emitted in process (3) with a transition probability $A_{10} (\text{s}^{-1})$. Through thermodynamic considerations of detailed balancing the rate coefficients k_{01} and $k_{10} (\text{cm}^3 \text{ s}^{-1})$ are related by

$$k_{01} = (g_1/g_0) k_{10} \exp(-h\nu/kT) \quad (4)$$

where k is Boltzmann's constant, T is the kinetic temperature and g_1 and g_0 are the statistical weights for the levels $v = 1$ and $v = 0$, respectively. Neglecting stimulated emission and induced absorption, a steady state condition for processes (1) to (3) corresponds to a concentration ratio

$$n(\text{NO}_{v=1})/n(\text{NO}_{v=0}) = k_{01}n(\text{M})/[k_{10}n(\text{M}) + A_{10}] \quad (5)$$

or, taking (4) into account

$$n(\text{NO}_{v=1})/n(\text{NO}_{v=0}) = (g_1/g_0) k_{10}n(\text{M})\exp(-h\nu/kT)/[k_{10}n(\text{M}) + A_{10}] \quad (6)$$

where $n(\text{NO}_{v=1})$, $n(\text{NO}_{v=0})$ are the concentrations of nitric oxide in the vibrational levels $v = 1$ and $v = 0$, and $n(\text{M})$ is the concentration of constituent M. Expression (6) shows that a dilution factor w representing a departure from a Boltzmann distribution is given by

$$w = k_{10} n(\text{M})/[k_{10} n(\text{M}) + A_{10}] \quad (7)$$

When the deactivation rate coefficient k_{10} is sufficiently large so that $k_{10}n(\text{M}) \gg A_{10}$, the population of the level $v = 1$ is given by a

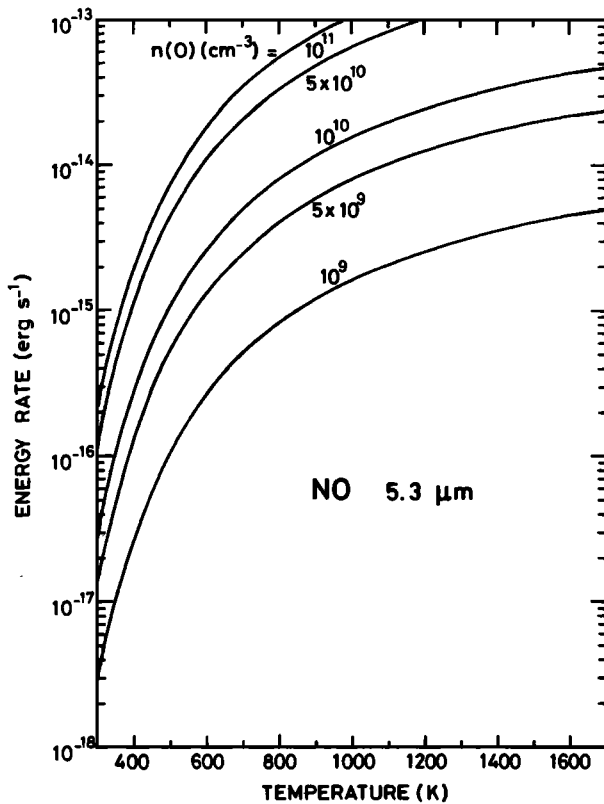


Fig. 1. Energy rate $L_{NO}/n(NO)$ as a function of temperature for various atomic oxygen concentrations. $k_{10}(O) = 6.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$.

Boltzmann distribution, since $w = 1$ in this case. Numerical calculations show that this condition is never satisfied for the $5.3 \mu\text{m}$ emission above 120 km altitude. As a consequence the nitric oxide fundamental band is not in local thermodynamic equilibrium and the cooling rate L_{NO} for an optically thin medium is given by

$$L_{NO} = hv n(NO_{v=1}) A_{10} = hv n(NO_{v=0}) w A_{10} (g_1/g_0) \exp(-hv/kT) \quad (8)$$

The integrated intensity of the NO fundamental band was found to be $135 \text{ atm}^{-1} \text{ cm}^{-2}$ at S.T.P. by King and Crawford (1972). With $g_1 = g_0$, such a value leads to a transition probability $A_{10} = 13.3 \text{ s}^{-1}$. Quenching of vibrationally excited nitric oxide by molecular oxygen and nitrogen has been measured by Murphy et al. (1975) who obtained $k_{10}(O_2) = 2.4 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ and $k_{10}(N_2) = 1.7 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$. Isotopic exchange of oxygen atoms with NO measured at 300 K by Herron and Klein (1964) leads to $k_{10}(O) = 1.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. Correcting the exchange rate for the isotopic substitution ratio, Klein and Herron (1964) suggest a rate coefficient $k_{10}(O) = 3.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ at 300 K. Glänzer and Troe (1975) measured a rate coefficient $k_{10}(O) = 3.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at 2700 K while Fernando and Smith (1979) obtained $k_{10}(O) = 6.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at 300 K. The highest value is adopted in the present work. It is clear that $k_{10}(N_2) < k_{10}(O_2) \ll k_{10}(O)$ and above 120 km only

atomic oxygen is considered as an efficient collisional partner in processes (1) and (2).

The energy rate $L_{NO}/n(NO_{v=0})$ computed with equation (8) is shown in Figure 1 as a function of temperature for various atomic oxygen concentrations which can be present between 120 km and 250 km altitude. The nitric oxide energy rate is strongly temperature dependent whereas the corresponding quantity for the $63 \mu\text{m}$ emission of atomic oxygen varies slowly between 5.8×10^{-19} and $8.8 \times 10^{-19} \text{ erg s}^{-1}$ for temperatures ranging from 300 K to 2000 K (Kockarts and Peetermans, 1970). Furthermore, the energy rate for the $5.3 \mu\text{m}$ emission of NO is always larger than for the $63 \mu\text{m}$ O emission. The dilution factor w ranges from 3.3×10^{-1} to 4.9×10^{-3} when $n(O)$ decreases from 10^{11} cm^{-3} to 10^9 cm^{-3} . The $5.3 \mu\text{m}$ emission is, therefore, never in local thermodynamic equilibrium.

Effect on the Thermopause Temperature

A simple estimate of the effect of nitric oxide cooling in the terrestrial thermosphere is obtained by solving the steady state heat conduction equation

$$dE/dz = P_{EUV} - L_O - L_{NO} \quad (9)$$

where $E = -\lambda dT/dz$ is the downward heat conduction flux, P_{EUV} is the extreme ultraviolet heat production rate, L_O and L_{NO} are the atomic oxygen and nitric oxide cooling rates, respectively. The heat conduction coefficient λ is taken from Banks and Kockarts (1973). Numerical integration of equation (9) requires a knowledge of lower boundary conditions at 120 km, EUV fluxes with their heating efficiency, absorption cross sections and a nitric oxide distribution. In order to consider a realistic case we adopt a nitric oxide profile measured simultaneously by a rocket-borne ultraviolet photometer and by a mass spectrometer (Trinks et al., 1978) on June 29,

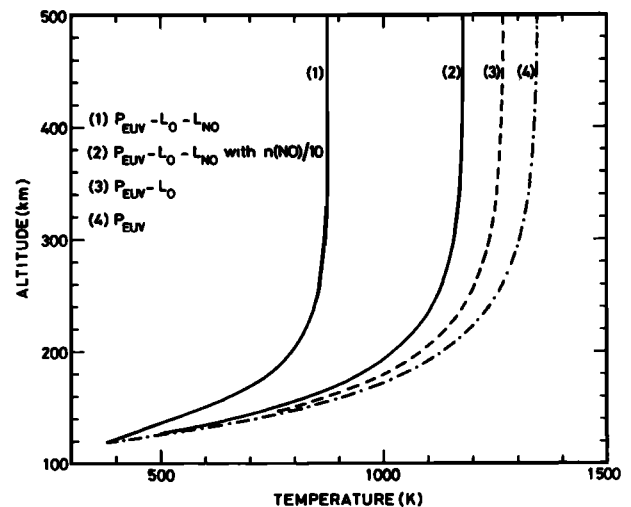


Fig. 2. Vertical distribution of thermospheric temperature. Numbers indicate which heating and loss processes are taken into account. Curve (2) indicates the effect of a reduction by a factor of 10 of the nitric oxide distribution used to compute curve (1).

1974 at 1514 local time. At 120 km the nitric oxide concentration is $4.6 \times 10^7 \text{ cm}^{-3}$ with a maximum of $6.2 \times 10^7 \text{ cm}^{-3}$ at 130 km. At the time and location of these measurements, the semi-empirical model DTM (Drag-Temperature-Model) of Barlier et al (1978) leads to the following conditions at 120 km: $T = 380 \text{ K}$, $n(O) = 5.69 \times 10^{10} \text{ cm}^{-3}$, $n(O_2) = 4.78 \times 10^{10} \text{ cm}^{-3}$ and $n(N_2) = 3.34 \times 10^{22} \text{ cm}^{-3}$ for a solar decimetric flux of $86 \times 10^{-22} \text{ W m}^{-2} \text{ Hz}^{-1}$, a mean flux of $87.2 \times 10^{-22} \text{ W m}^{-2} \text{ Hz}^{-1}$ and a geomagnetic index $K_p = 2.66$. For a solar decimetric flux of $95 \times 10^{-22} \text{ W m}^{-2} \text{ Hz}^{-1}$ Schmidtke (1976) measured a total EUV flux of $3.37 \text{ erg cm}^{-2} \text{ s}^{-1}$ which is used in equation (9) with a heating efficiency of 0.37, a unique absorption cross section of $1 \times 10^{-17} \text{ cm}^2$ and a solar zenith angle $\chi = 43.6^\circ$.

The temperature resulting from the integration of the steady state heat conduction equation (9) is shown in Figure 2. Without any loss process except downward heat conduction (curve P_{EUV}), the thermopause temperature reaches a value of 1350 K. The introduction of nitric oxide cooling reduces the thermopause temperature to 910 K and the addition of the $63 \mu\text{m}$ O cooling produces a further reduction of 35 K leading to a steady state temperature of 875 K (curve $P_{EUV} - L_O - L_{NO}$). The $63 \mu\text{m}$ cooling effect (curve $P_{EUV} - L_O$) is computed for an optically thick atmosphere where the reduction factor introduced by Kockarts and Peetermans (1970) is approximated by the empirical expression given by Glenar et al. (1978). It is clear from Figure 2 that nitric oxide cooling is a very efficient process. At 120 km altitude the temperature gradient decreases from 20K/km with P_{EUV} alone to 6 K/km when nitric oxide and atomic oxygen are introduced.

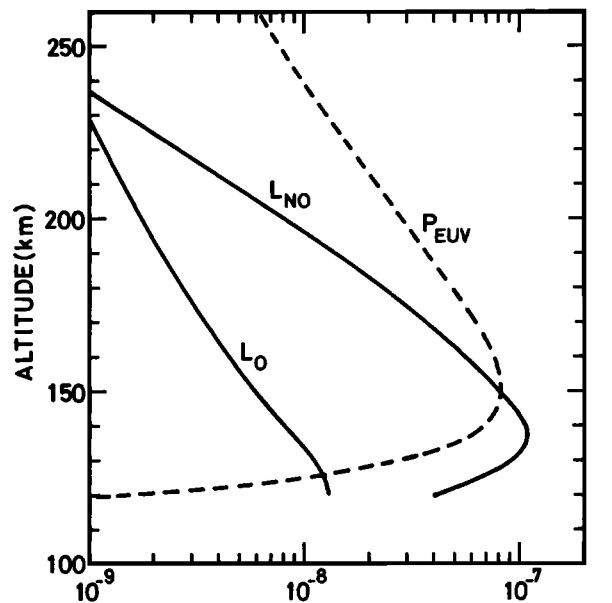
Figure 2 shows also the temperature profile (curve (2)) obtained when the nitric oxide concentration of Trinks et al. (1978) is arbitrary reduced by a factor of 10.

The production and loss terms of the energy equation are shown in Figure 3 where it appears that L_{NO} is more important than L_O and can even exceed P_{EUV} . Since the energy rate $L_{NO}/n(\text{NO})$ (see figure 1) is an increasing function with height, the volume energy loss rate L_{NO} is characterized by a maximum which is at 140 km in the present case.

Discussion

In a calculation of the $5.3 \mu\text{m}$ excitation Ogawa (1976) uses the low value $k_{10}(O)$ of Herron and Klein (1964) up to 120 km, whereas Gordiets et al. (1978) use between 90 and 250 km the high value at 2700 K obtained by Glänzer and Troe (1975). The high value of Fernando and Smith (1979) leads to a maximum emission of $1.1 \times 10^7 \text{ erg cm}^{-3} \text{ s}^{-1}$ at 140 km while Gordiets et al. (1978) find $2 \times 10^7 \text{ erg cm}^{-3} \text{ s}^{-1}$. Observed $5.3 \mu\text{m}$ emission of NO can be higher than values deduced from Figure 3 since resonant excitation by solar and/or earth's radiation contributes to the $5.3 \mu\text{m}$ emission but is not introduced in the thermospheric heat budget. Integration of L_{NO} given in Figure 3 leads to an apparent emission of 1.2 MR.

Theoretical calculations (Oran et al., 1975;



ENERGY PRODUCTION AND LOSS ($\text{erg cm}^{-3} \text{ s}^{-1}$)

Fig. 3. Height distribution of the energy production and loss rates involved in the computation of Fig. 2 using the NO distribution of Trinks et al. (1978).

Strobel et al., 1976; Ogawa and Kondo, 1977) clearly show large diurnal variations of nitric oxide. These results combined with the strong temperature dependence of the nitric oxide cooling indicate that the decrease of the order of 500 K in the temperature obtained in Figure 2 should be considered as indicative. The actual effect must be analyzed for various conditions of the thermosphere. Nevertheless a reduction by a factor of 10 of the NO distribution measured by Trinks et al. (1978) still leads to a significant effect (see curve (2) in Figure 2).

High-latitude nitric oxide measurements (Gérard and Barth, 1977) show that auroral activity may lead to an NO density increase by a factor of eight. Rees and Roble (1979) predict NO increases during auroral electron precipitations. Under such disturbed conditions it is suggested that nitric oxide cooling plays a regulating role above 120 km in order to avoid unrealistic temperature increases in the thermosphere.

Since carbon dioxide seems to be the major thermospheric cooling agent below 120 km (Kockarts 1975; Alcaydé et al. 1979) and since nitric oxide cooling appears as a major effect above 120 km, it is not excluded that the initially assumed atomic oxygen cooling is actually a minor process in many cases. A systematic introduction of nitric oxide cooling is, however, not straightforward since the nitric oxide distribution depends on the thermal structure and on the composition of the thermosphere. Such a situation can be compared to the case of the homosphere where the thermal structure is also strongly influenced by trace constituents.

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