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A DETAILED EVALUATION OF HEATING PROCESSES IN THE MIDDLE ATMOSPHERE

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1. INTRODUCTION

A fundamental problem in the study of the terrestrial middle atmosphere is to calculate accurately the local heating due to the absorption of solar radiation. Knowledge of the heat budget is essential to understanding the atmospheric thermal structure, atmospheric motions, atmospheric chemistry, and their coupling. The evaluation of heating rates is complicated (especially above the stratopause) by the fact that the heating is not a simple one-step process. That is, the absorbed solar energy does not all immediately appear as heat. Rather, substantial portions of the incident energy may appear as internal energy of excited photolysis products (e.g., $O(^1D)$ or $O_2(^1\Delta)$) or as chemical potential energy of product species such as atomic oxygen. The ultimate disposition of the internal and chemical energy possessed by the photolysis products determines the efficiency and thus the rate at which the middle atmosphere is heated. In studies of the heat budget, it is also vitally important to consider transport of long lived chemical species such as atomic oxygen above ~ 80 km. In such cases, the chemical potential energy may be transported great distances (horizontally or vertically) before undergoing a reaction to release the heat. Atomic oxygen influences the heating not only by reactions with itself and with O_2 but also by reactions with odd-hydrogen species, especially those involving OH [Mlynczak and Solomon, 1991a]. Consequently, absorbed solar energy may finally be converted to heat a long time after and at a location far from the original deposition.

The purpose of this paper is to examine the solar and chemical heating processes and to present parameterizations for the heating efficiencies readily applicable for use in numerical models and heat budget studies. In the next two sections the processes relevant to the heating efficiencies for ozone and molecular oxygen will be reviewed. In Section 4 the processes for the exothermic reactions will be reviewed and parameterizations for the heating efficiencies for both the solar and chemical processes will be presented in Section 5.

2. CALCULATION OF THE SOLAR HEATING EFFICIENCIES FOR OZONE

In this section we develop the formalism for evaluating the heating efficiencies for absorption of solar ultraviolet radiation by ozone. Ozone is dissociated through the absorption of ultraviolet and visible radiation in three bands; the Hartley band (200-300 nm), the Huggins band (310-350 nm), and the Chappuis bands (450-850 nm). The Hartley band is the most significant in terms of heating rate above the stratopause, while all three bands are very important in the

middle and lower stratosphere and the troposphere. Excited photolysis products are generated only by photolysis in the Hartley band. As discussed below, this fact implies that the heating in the Huggins and Chappuis bands occurs at unit efficiency.

Ozone is dissociated by absorption in the Hartley band into one of two "channels"

$$O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta) \qquad (1)$$

$$O_3 + h\nu \rightarrow O(^3P) + O_2(^3\Sigma, \upsilon) \qquad (2)$$

The "channel" corresponding to Eq. 1 is called the singlet channel in reference to the spin state of the excited oxygen photolysis products. By analogy, the "channel" corresponding to Eq. 2 is called the triplet channel, since triplet oxygen species are formed. Note that the molecular oxygen in the triplet channel may be produced in a vibrationally excited form [Slanger et al., 1988], hence the script υ in the notation.

We define the heating efficiency at a given altitude in general terms as the difference between the energy available for heat and the energy lost due to airglow emission, relative to the energy available for heat. That is,

$$\varepsilon = \frac{(E_\nu - E_b) - E_\Re}{E_\nu - E_b} \qquad (3)$$

where E_ν is the energy of the incident solar photon, E_b is the energy required to break the chemical bonds of ozone, and $E_\Re$ is the energy lost by radiative emission (airglow). The quantity $(E_\nu - E_b)$ is the energy immediately available for heat. As a consequence of this definition, any heating process in which there is no radiative loss (i.e., $E_\Re = 0$) will have an efficiency of 1.0 as is assumed for the triplet channel of ozone photolysis.

The quantum yields for the singlet and triplet channels are about 0.9 and 0.1, respectively, indicating that the singlet channel is by far the dominant pathway for ozone photolysis. The detailed processes by which the singlet and triplet channels relax are discussed in Mlynczak and Solomon, [1991b] and in Mlynczak and Solomon [1992]. In general, some of the $O(^1D)$ energy is converted to internal energy of O_2, forming $O_2(^1\Sigma)$, which then radiates. Loss from $O_2(^1\Delta)$ is also quite significant. Based on the work of Harris and Adams [1983], we conclude that energy transfer from $O(^1D)$ to N_2 to CO_2 followed by emission by CO_2 at 4.3 μm is only a minor source of energy loss below 100 km.

Before discussing the efficiency calculations we must first consider the disposition of the energy radiated by $O_2(^1\Delta)$ and $O_2(^1\Sigma)$. If sufficient optical mass is present, radiative energy lost from the volume in which the excited species was generated may be absorbed in another other volume some distance away. In such instances, the net gain or loss of photons must also be determined to calculate the local heating. Based on calculations of the escape function [e.g., Andrews et al., 1987] we find that all radiation emitted by $O_2(^1\Delta)$ and $O_2(^1\Sigma)$ either escapes to space or is absorbed in the dense atmosphere with negligible heating upon absorption.

Under steady-state conditions, it is relatively straightforward to show that the heating efficiency is virtually independent of the quantum yield, the ozone concentration, and the photolysis rate. In fact, the efficiency is dependent only on the kinetic and spectroscopic parameters describing the relaxation of the excited species and on the energies of the photons radiated by $O_2(^1\Delta)$, $O_2(^1\Sigma)$, the incident photon energy, and the dissociation energy. This fact will be very important when developing parameterizations of the heating efficiency for use in numerical models.

The heating efficiency for the Hartley band is presented in Figure 1. Below about 50 km, the efficiency is equal to one implying that all internal energy is generated in the singlet channel is locally quenched to release heat.
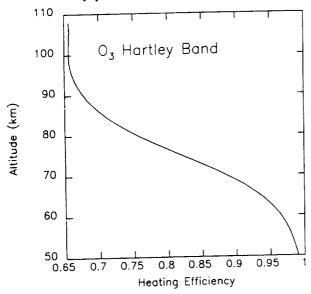

Fig. 1 The heating efficiency of the Hartley band of ozone.

3. HEATING EFFICIENCIES FOR THE PHOTOLYSIS OF MOLECULAR OXYGEN

We turn now to the heating efficiencies associated with the photolysis of molecular oxygen which is dissociated through the absorption of solar ultraviolet radiation in four systems, the Herzberg system, the Schumann-Runge bands, the Schumann-Runge continuum, and the Lyman-alpha band. Only photons in the Schumann-Runge continuum and in the Lyman-alpha band are sufficiently energetic to produce excited atomic oxygen upon dissociation, with one $O(^1D)$ atom and one $O(^3P)$ atom being produced per each photolysis event [Brasseur and Solomon, 1986] in each system. For the altitudes under consideration ($z < 115$ km), radiative loss from $O(^1D)$ is negligible [Harris and Adams, 1983]. Consequently, the only mechanism by which the heating efficiency can be

reduced is by energy transfer to radiatively active species. The $O(^1D)$ energy generated by O_2 photolysis will undergo energy transfer processes identical to that for the $O(^1D)$ generated by O_3 photolysis. Energy can be lost by emission from $O_2(^1\Sigma)$, $O_2(^1\Delta)$, and $CO_2(001)$.

Shown in Figures 2 and 3 are the heating efficiencies for both the Schumann-Runge continuum and the Lyman-alpha band. In both cases illustrated here, it has been assumed that there is negligible loss from emission by CO_2. These figures demonstrate that very little energy is lost when Lyman-alpha radiation dissociates molecular oxygen in the region where such dissociation is significant (80-100 km), the efficiencies being greater than about 94%. The heating efficiency in the Schumann-Runge Continuum is smaller than in Lyman-alpha band even though both systems produce the same excited photolysis product $O(^1D)$. This apparent contradiction is due to the fact that the amount of energy immediately available for heat ($E_v - E_b$) is larger in the case of Lyman-alpha photolysis than in the Schumann-Runge Continuum.
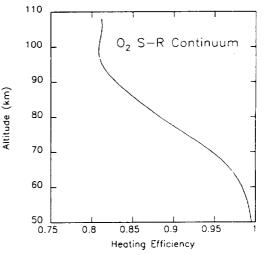

Fig. 2 The heating efficiency of the Schumann-Runge continuum of molecular oxygen.
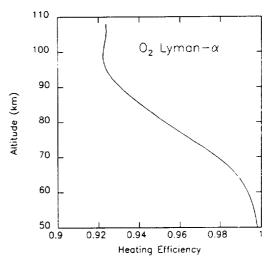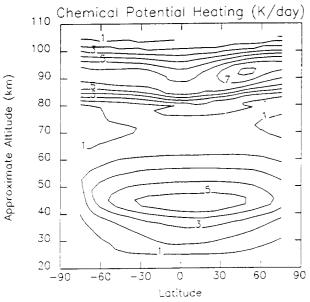

Fig. 3 The heating efficiency in the Lyman-alpha band of molecular oxygen.
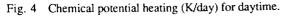
4. HEATING DUE TO EXOTHERMIC CHEMICAL REACTIONS

As discussed above, not all of the absorbed solar energy appears as heat in the atmosphere but rather substantial portions of the incident energy are converted to chemical form. This chemical energy is realized as heat during exothermic reactions which take place subsequent in time and potentially far away in space from the location of the initial photon deposition.

Using the constituent concentration fields calculated by the Garcia and Solomon two dimensional model [Garcia and Solomon, 1983; 1985] we have calculated the potential heating rate in Kelvin per day for seven exothermic reactions identified [e.g., Mlynczak and Solomon, 1991a] as being responsible for depositing substantial amounts of heat in the terrestrial middle atmosphere. The latitudinal distribution of the total chemical potential heating from these reactions (at equinox) is shown in Figures 4 and 5. From Figure 4 it can be seen that exothermic reactions are important from the lower stratosphere to the lower thermosphere. Below 60 km, the heating is due almost entirely to the reaction of O and O_2 which forms ozone. Above 60 km, all reactions contribute to the heating. The chemical heating at night (Figure 5) shows a strong contrast to the daytime heating rate. First, there is virtually no chemical heating below ~ 80 km because of the disappearance of atomic oxygen and atomic hydrogen. Secondly, the chemical heating above 80 km is much larger at night owing to the increase in ozone which fuels the fast reaction with atomic hydrogen.

The heating rates in Figures 4 and 5 represent the maximum possible heating based on the model constituent concentrations and reaction rates. The actual heating may be much less than the potential heating rate if any of the reaction products are radiatively active and excited to any extent by the reaction. Chemiluminescent emission is a significant source of energy loss from the atmosphere, particularly in from vibrationally excited OH and possibly from vibrationally excited O_3 [Mlynczak and Solomon, 1991a; Mlynczak 1991]. The energy loss associated with chemiluminescent emission is analogous to the airglow loss discussed for direct solar heating in that it effectively reduces the heating efficiency of the individual reaction.
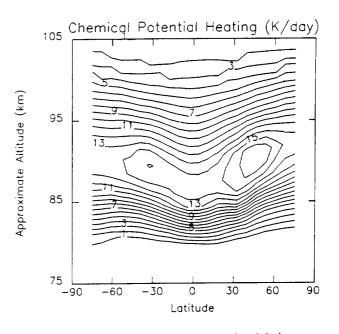

Fig. 4   Chemical potential heating (K/day) for daytime.

Fig. 5   Chemical potential heating (K/day) for nighttime.

5. HEATING EFFICIENCY PARAMETERIZATIONS

We conclude with a parameterization of the heating efficiencies for the three solar heating processes and the two chemical reactions with potentially significant chemiluminescent emission. For solar heating, the efficiencies are virtually independent of the photolysis rate and of the absorber (i.e., O_3 or O_2) concentration. The chemical heating efficiency is virtually independent of the reactant concentrations and of the rate of reaction. In both cases, the calculated efficiency depends strongly on the kinetic and spectroscopic parameters which describe the removal of energy from from the excited product molecules. The rates and mechanisms of energy removal are reasonably well known for the quenching of $O(^1D)$, $O_2(^1\Delta)$, and $O_2(^1\Sigma)$ so that the solar heating efficiencies are calculated with a high degree of confidence. In addition, Mlynczak and Solomon [1991b] demonstrated good agreement between calculated efficiencies and those inferred from airglow observations. The quenching rates and mechanisms of vibrationally excited OH and O_3 are not nearly as well known as are the rates for the oxygen species formed in photolysis events. Consequently, there is uncertainty in the efficiencies which we recommend for the exothermic reactions. The recommended efficiencies are based upon using the latest quenching rates that have been measured in laboratory and reported in the literature.

We have parameterized the heating efficiency in the Hartley band of ozone as a function pressure by fitting a fifth degree Chebyshev polynomial to the efficiency curve shown in Figure 1. The efficiency on a given pressure surface between 10^{-4} mb and 1.0 mb can be accurately calculated by the following expression

$$\varepsilon(x) = c_0 + c_1 x + c_2 x^2 + c_3 x^3 + c_4 x^4 + c_5 x^5 \qquad (4)$$

where the parameter x is defined by

$$x = \frac{(\log_{10}p + 2)}{2} \qquad (5)$$

and p is in mb. The values of constants c_0 through c_5 are 0.75985, 0.29536, 0.13921, - 0.17906, - 0.07893, and - 0.05123, respectively. Calculations of the efficiency using these equations agree with the efficiencies calculated from the detailed kinetics to within 0.5 percent at all pressure levels within the indicated range. The evaluation of the efficiency using this parameterization requires about 15 floating point operations per pressure level, roughly 2.5 times less the number of operations required for direct evaluation using the detailed kinetics. For reference, the efficiencies at 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}, and 10^0 mb are 0.6526, 0.6627, 0.7598, 0.9166, 0.9876, respectively.

For photolysis of molecular oxygen in the Schumann-Runge continuum, Mlynczak and Solomon [1991b] showed that the heating efficiency is about 0.87 between 95 and 110 km considering only radiative loss from $O_2(^1\Sigma)$ and $O_2(^1\Delta)$. This initial calculation was based on an estimated Schumann-Runge continuum photon at 150 nm. We have revised our recommended efficiency using an actual calculation of the mean photon wavelength (172 nm) in addition to incorporating the Harriss and Adams [1983] $O(^1D)$ thermalization profile to account for $CO_2(001)$ loss. We now recommend an efficiency of 0.78, constant with altitude, between 85 and 110 km.

It suffices to simply use a constant efficiency of 0.93 at all altitudes in order to parameterize the heating efficiency of Lyman-alpha radiation. This approximation results in an error of less than 0.01 K/day in the Lyman-alpha heating rate and an error of less than 1 % in the total heating rate at any altitude.

Based on the recent determinations of the quenching rates of OH by O_2 [Dodd et al., 1991], the Einstein coefficients of Nelson et al. [1990], and the reaction rate of OH(1) with O, [Spencer and Glass, 1977], we recommend a heating efficiency of 0.6, constant with altitude over the 80-100 km region, for the reaction of atomic hydrogen with ozone. The efficiency can approach 0.65 to 0.80 if the rate constants derived from OH airglow observations are employed (e.g., those utilized in Lopez-Moreno et al., [1987]). It is a fact that laboratory measurements of the OH quenching rates (e.g., Streit and Johnston, 1976 and Dodd et al., 1991) are generally much smaller than those inferred from airglow measurements. It is also quite likely that interactions between atomic oxygen and vibrationally excited hydroxyl are very important in determining the overall heating efficiency. However, rate constants for such processes are unknown.

The situation is similar with regard to the quenching of vibrationally excited ozone. There have been two different models used in the analysis of ozone limb emission data [Solomon et al., 1986; Rawlins, 1985]. The Rawlins model has a very strongly quenched ozone molecule, while quenching is very weak in the Solomon et al. model. Application of these two models yields much different heating efficiencies [Mlynczak, 1991]. In order to be consistent with our recommendations above, we recommend a unit heating efficiency for the reaction of atomic and molecular oxygen to form ozone. This is based on the laboratory work of Rawlins and Armstrong, [1987] which showed that only about 25% of the available chemical energy is converted to internal energy of ozone, most of which is quenched to release heat.

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