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ROLE OF CARBON DIOXIDE IN COOLING PLANETARY THERMOSPHERES

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Abstract. A new value of the rate coefficient for the deactivation of the bending mode of carbon dioxide by atomic oxygen at low temperatures is derived from the observation of 15 μm emission from the atmosphere of the Earth. This new value gives a cooling rate for the lower thermosphere that is two to three times the rate previously calculated, and it may resolve a long-standing problem in the Mars-Venus aeronomy.

Introduction

The role of carbon dioxide in cooling the thermospheres of Earth, Venus, and Mars is well recognized [Gordiets et al, 1982, Dickinson, 1984, Dickinson et al, 1987; Dickinson and Bougher, 1986, Bougher and Dickinson, 1988]. During a collision of CO_2 with atomic and molecular species, some of the translational energy of relative motion (heat) is converted into vibrational energy of the lowest-lying mode, the bending mode, ν_2. This vibrational energy is subsequently radiated at 15 μm. Many of these photons escape to space, cooling the atmosphere. A critical parameter in this process is the rate coefficient for the deactivation of the bending mode by atomic oxygen. Taylor [1974] gives its value as $2.32\times10^{-9}\exp(-76.75/T^{1/3})$ cm^3/mol-s. This expression has the standard Landau-Teller form and is obtained by extrapolation from high-temperature shock-tube experiments. There are no low-temperature measurements, however, and the rate constant is considered to be very uncertain.

We suggest that a revised value,

$$k_O = 3.5(\pm 1.8)\times 10^{-13}\sqrt{T} + 2.32\times 10^{-9}\exp(-76.75/T^{1/3}) \qquad (1)$$

better represents the overall temperature behavior and should be used for atmospheric studies. This revised value is larger than that given by Taylor by a factor of 1070 at 200 ^{0}K and by a factor of 54 at 500 ^{0}K. At 300 ^{0}K it equals 6×10^{-12} cm^3/mol-s. Sharma and Nadile [1981] in a preliminary study proposed 5×10^{-13} for this rate constant at room temperature. Values close to this have since been used in the literature [Gordiets et al, 1982; Roble et al, 1987; Dickinson and Bougher, 1986; Kumer and James, 1982]. The value being proposed in this article is about 12 times larger than the preliminary value and is closer to results from the expression $2\times10^{-13}\sqrt{T}$ given by Sharma [1988] for low temperatures.

Enhanced emission resulting from a large upward revision of this rate coefficient affects the modeling of the mesosphere and lower thermosphere of the Earth. The impact on the understanding of the energy budget of Venus may, however, be dramatic. The upper atmospheres of Venus and Mars are composed mainly of CO_2, with small admixtures of O, CO, and O_2/N_2 in decreasing proportion [Chamberlain and Hunten, 1987]. While the thermospheric temperature structure is reasonably well understood for Mars, the corresponding understanding for Venus, which has a similar atmosphere, is lacking [Fox and Bougher, in press, 1990]. (The major compositional difference is the mixing ratio of O, ~1% at the Martian homopause [Neir and McElroy, 1977] compared to about 6-8% on Venus [Hedin et al, 1983].) Fox [1988] has calculated large EUV heating efficiencies (16-25%) for Venus which, in turn, result in predictions of the exospheric temperature that are much too high.

Recently Keating and Bougher [in press, 1990] have pointed out that the response of the Venus thermosphere to short-term solar variations can only be explained by very strong cooling in the 15 μm bands, and not by very large eddy cooling [cf. Hollenbach et al, 1985]. They also point out that the heating efficiency calculated by Fox [1988] together with the rate coefficient k_O proposed here yield a reasonable model for the Venetian thermosphere.

SPectral Infrared Rocket Experiment

SPIRE was launched from the University of Alaska's Poker Flat Research Range shortly before dawn on September 28, 1977, into a quiescent non-auroral atmosphere [Stair et al, 1985]. For about five minutes it measured limb emission in the spectral range 1.4-16.5 μm. It made twelve spatial scans. Scans 1-7 were terminator scans for which the lines of sight (LOS) were partially sunlit, scan 8 was a night-time scan, and scans 9-12 had LOS completely sunlit.

A plot of radiance in the ν_2 band of CO_2 as a function of tangent height shows several features, of which two are worthy of special notice. (1) Within the scatter of the data, the day and night measurements do not show any systematic differences. In other words the 15 μm emission, early in the morning, is independent of whether the LOS are dark or sunlit. (2) The band radiance remains nearly constant as the tangent height increases from about 94 to 110 km. This is important, because according to all models of the atmosphere the CO_2 density should decrease by a factor of at least thirty in this altitude range. Recalling the fact that the radiance observed on any tangent path originates primarily at the tangent altitude, and ignoring small effects due to self-absorption, we conclude that the excited state density stays almost constant, or the ratio of the densities of the upper radiating state (01^10) to the lower radiating state (00^00) of CO_2 increases by a factor of thirty or more, as we go from 94 to 110 km.

Model of the 15 μm Emission from CO_2

We recall the observation that solar radiation, early in the morning, does not play an important role in the emission process at 15 μm. Consider the ground and first excited states, 00^00 and 01^10. The molecules in the upper state are produced from those in the lower state by collisions with N_2, O_2, and O and by absorption of the upwelling radiation from the atmosphere (earthshine). The upper-state molecules N_u are converted to the lower-state molecules N_l by collisions with N_2, O_2, and O and by

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spontaneous emission. The steady-state equation for the two-level system may then be written as

$$N_u/N_l = (J + kK)/(A + k) \quad (2)$$

where J is the pumping rate due to earthshine, A is the Einstein coefficient for spontaneous emission, $k = \sum k_M[M]$ and kK are the collisional de-excitation and excitation rates of the upper state, $K = 2\exp(-960/T)$ is the equilibrium constant (960 °K being the energy separation of the two levels), T is the translational temperature, and the factor of two in the expression for K arises from the ratio of statistical weights of the upper and lower states.

The rate of collisional deactivation of 01^10 by N_2 and O_2 has been measured in the temperature range of interest [Allen et al, 1980; Lunt et al, 1985; Simpson et al, 1977; Taine et al, 1978; Taine and Lepoutre, 1979]. The contribution of atomic oxygen has already been mentioned. It is the computation of J that forms the heart of the calculation. As the upwelling radiation leaves the lower atmosphere, the photons at the line centers of strong bands, like the one under discussion, are rapidly absorbed or bleached out. A large fraction of the radiation contributing to J comes from the line wings. The radiative transfer calculation must be carried out carefully, taking into account changes in the lineshape and the absorption coefficient as the temperature and density change with altitude. We wrote an accurate line-by-line code, called RAD, for the purpose of calculating J [Wintersteiner et al, 1988]. The code assumes a one-dimensional plane-parallel atmosphere and that the spectral lines do not overlap. It equates the rotational temperature with the translational temperature and assumes that an absorbed photon may be emitted anywhere in the line with a probability determined by the shape of the line. RAD calculates the vibrational temperature from the logarithm of the right-hand side of Eq. (2), iteratively.

Model Atmosphere

Since the rocket was at approximately 285 km while the measurements were being made, in-situ measurements of the atmospheric parameters could not be carried out. We used the MSIS-86 thermospheric model [Hedin, 1987] to give the temperature, densities of N_2, O_2, and O, and the total density under the SPIRE conditions. Below the 85-km lower boundary of MSIS, the sub-arctic winter atmosphere given in FASCODE [Anderson et al, 1986] was used, with suitable interpolation near the boundary. We were able to correctly reproduce the rotational profile of the 15 μm band using the temperature thus obtained, giving some credibility to this procedure. For [O] we used a simple extrapolation of the MSIS profile below 85 km. Figure 1 shows [O] as a function of altitude.

To estimate [CO_2] we determined mixing ratios from all thermospheric measurements reported in the literature. Above 110 km, the measurements are in general agreement, but in the altitude range 80-110 km there is a disparity between the results of rocket experiments [Trinks and Fricke, 1978; Trinks et al, 1978; Offermann et al, 1981; Offermann and Grossmann, 1973] and satellite experiments [Vercheval et al, 1986; Girard et al, 1988; Beer et al, 1987], with the former measurements consistently showing up to 50% more CO_2 than the latter. We represented the data with two smoothed mixing ratio profiles and ran the model using CO_2 densities, shown in Figure 1, that were derived from each of them. Curve D refers to the profile derived from the rocket data, and curve E to that from satellite data.

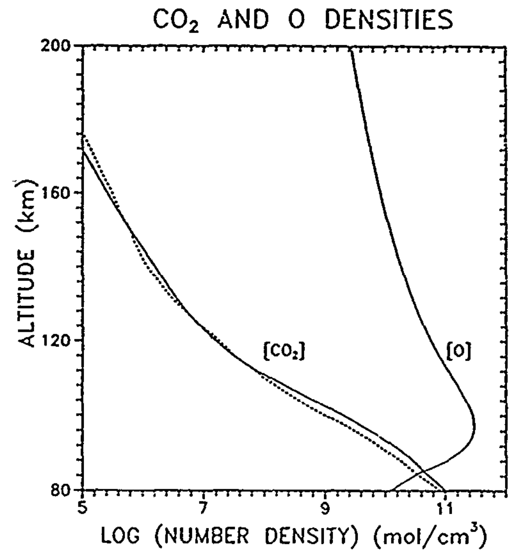

Fig. 1. Atomic oxygen and carbon dioxide densities as a function of altitude. The [O] profile is from MSIS-86; [CO_2] curves D (solid line) and E (dashed line) are approximations to rocket and satellite measurements, respectively.

Comparison of Measured and Calculated Radiances

After computing the vibrational temperatures, we used a line-by-line radiative transport code, NLTE [Wintersteiner and Sharma, 1985], to compute the limb radiance in each rotational line of the 01^10—00^00 vibrational bands of the four most important isotopes of CO_2. RAD and NLTE were also used to compute the limb radiance from four hot bands (03^30→02^20, 10^00→01^10, 02^00→01^10, 02^20→01^10) of the most abundant isotope, $^{12}C^{16}O_2$ and from the 02^20→01^10 band of $^{13}C^{16}O_2$. At 85 km tangent height the major and minor isotopes make equal contributions to the radiance in the 13-16.5 μm wavelength interval because of greater self-absorption of radiation from the most abundant isotope. Above 105 km, however, only the 01^10—00^00 transition of the most abundant isotope makes a significant contribution to the radiance at 15 μm.

We ran the model using the two CO_2 profiles and compared the predicted limb radiance with the SPIRE dataset. The 94-110 km feature discussed earlier is due to the efficiency with which O-atom collisions excite the bending mode. this is exactly the region where [O] and k_O increase rapidly with altitude. It is impossible to reproduce this feature with accepted values of the rate constant, so we let k_O (or, more precisely, the coefficient of $\sqrt{T}$ in Eq. (1)) be a free parameter. Figures 2 and 3 compare the measured radiance with three radiance profiles, calculated with different O-atom rate constants having the form $A \times 10^{-13}\sqrt{T} + 2.32 \times 10^{-9}\exp(-76.75/T^{1/3})$. The best overall description of the observations is obtained with a value $A \sim 3.5$.

Sensitivity to Model Input

In our model, [O] and k_O appear only as a product, so any error in the former is immediately reflected in the result we obtain for the latter. Although [O] is quite variable, the standard deviations between the MSIS-86 model and lower-thermosphere data reportedly range up to about 30% [Hedin, 1988]. If the MSIS predictions were known to be in error by substantially more than this, our error estimate for k_O would have to be correspondingly revised.

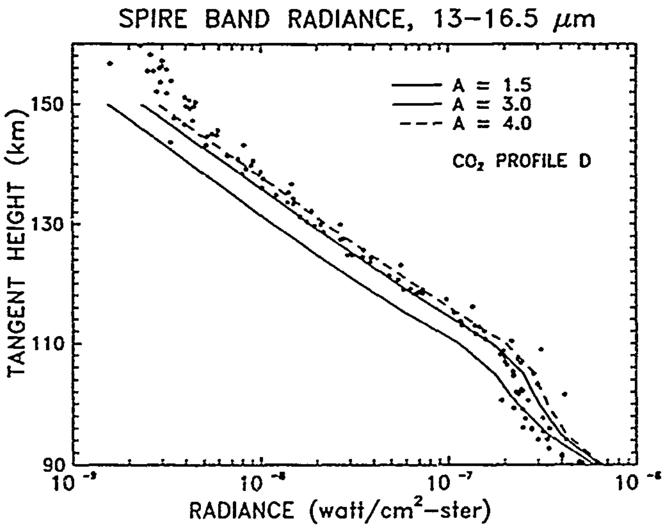

Fig. 2. Limb radiance in the 13.0-16.5 μm band as a function of tangent height. Asterisks denote the SPIRE measurements. The calculated radiances use CO_2 profile D. The parameterization for k_O is $A \times 10^{-13}\sqrt{T} + 2.32 \times 10^{-9} \exp(-76.75/T^{1/3})$, and the values used for A are indicated.

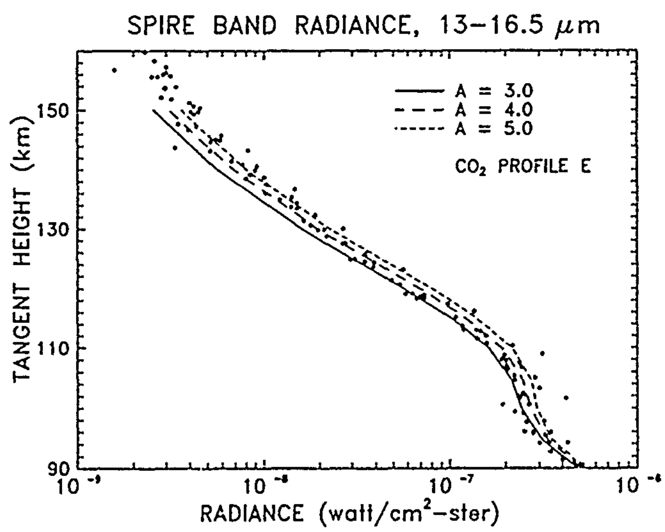

Fig. 3 As Figure 2, but the radiances were calculated using CO_2 profile E.

Above 110 km, the limb radiance is proportional to the CO_2 column density on the viewing path. In this altitude range the mixing ratio dataset has a standard deviation of about 25% about the mean. Test runs show that a 25% change in $[CO_2]$ is compensated by a change of approximately 36% in k_O. For lower tangent paths, even though the uncertainty in $[CO_2]$ is greater, self-absorption sharply diminishes the sensitivity of the limb radiance to the column density.

The limb radiance in the thermosphere is also sensitive to the temperature profile, particularly to the mesopause temperature. We ran our model with two FASCODE atmospheres [Anderson et al, 1986] having lower and higher mesopause temperatures. Radiance results obtained using the midsummer profile, with a cold mesopause, are consistent with the experimental data when k_O is given by Eq. (1) However, results obtained with the midwinter profile, with a warmer mesopause, do not match the experiment and cannot be reconciled with it by adjusting k_O downward. This indicates that the temperature profile is at least approximately correct, and that k_O cannot be greatly in error on this account.

The overall effect of the major uncertainties in model input leads to an error of approximately 50% in the rate coefficient, as given in Eq. (1).

Cooling Rates

Figure 4 gives the cooling rate due to 15 μm emission as a function of altitude for both CO_2 profiles. Below 120 km this is the principal cooling mechanism. Since it is very sensitive to k_O, these results represent a substantial increase over cooling rates previously reported [cf. Dickinson, 1984]. This has important implications for the transport of heat into and within the lower thermosphere, and for its thermal balance as well.

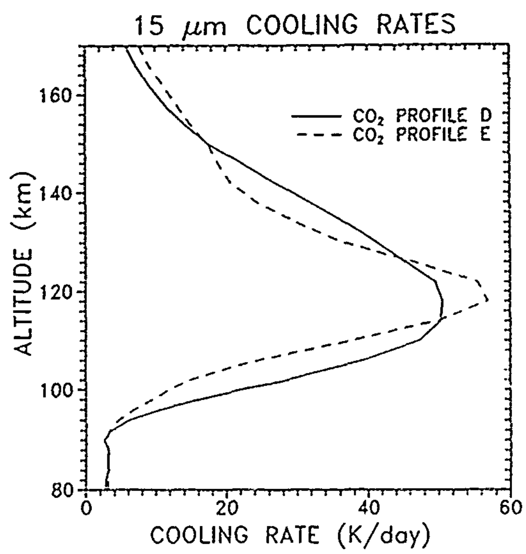

Fig. 4. Cooling rates due to 15 μm emission from the Earth's atmosphere, as a function of altitude, for both CO_2 profiles.

Summary

Based upon observations of 15 μm emission from the atmosphere of the Earth, we have deduced a new value for the rate of deactivation of the bending mode of carbon dioxide by atomic oxygen. Using this rate coefficient we calculate cooling rates for the terrestrial thermosphere that are larger than generally recognized. This will also give larger cooling rates for the Venus thermosphere, and possibly resolve the long-standing problem regarding its temperature structure.

Because of its extremely important role in cooling planetary thermospheres, it is of great interest to obtain independent confirmation of these low-temperature results in the form of laboratory measurements.

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