AD-A230 256

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION	1b RESTRICTIVE MARKINGS
Unclassified	
2a. SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT
	Approved for public release; Distribution
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	unlimited

4 PERFORMING ORGANIZATION REPORT NUMBER(S)	5 MONITORING ORGANIZATION REPORT NUMBER(S)
GL-TR-90-0342	

6a NAME OF PERFORMING ORGANIZATION	6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION
Geophysics Laboratory	OPS	

6c ADDRESS (City, State, and ZIP Code)	7b ADDRESS (City, State, and ZIP Code)
Hanscom AFB Massachusetts 01731-5000	

8a NAME OF FUNDING/SPONSORING ORGANIZATION	8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c ADDRESS (City, State, and ZIP Code)	10 SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO
	63220C	S321	13	01

11 TITLE (Include Security Classification)
Role of Carbon Dioxide in Cooling Planetary Thermospheres

12 PERSONAL AUTHOR(S)
Ramesh D. Sharma, Peter P. Wintersteiner*

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Reprint	FROM ____ TO ____	1990 December 20	4

16 SUPPLEMENTARY NOTATION *ARCON Corp
Reprinted from Geophysical Research Letters, Vol. 17, No. 12, pages 2201-2204, November 1990

17	COSATI CODES		18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Carbon dioxide, atomic oxygen, 15 micron emission, Atmosphere of the Earth, Cooling rate

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Abstract. A new value of the rate coefficient for the de-activation 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.

Accession

NTIS GRA&I
DTIC TAB
Unannounced
Justification

By
Distribution/
Availability Codes

Dist	Avail and/or Special
A-1	20

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS	Unclassified
22a NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c OFFICE SYMBOL
Ramesh D. Sharma	(617) 377-4198	OPS

DD Form 1473, JUN 86   Previous editions are obsolete.   SECURITY CLASSIFICATION OF THIS PAGE

ROLE OF CARBON DIOXIDE IN COOLING PLANETARY THERMOSPHERES

Ramesh D. Sharma
Geophysics Laboratory

Peter P. Wintersteiner
ARCON Corp.

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 $2.32 \times 10^{-9} \exp(-76.75/T^{1/3})$ 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 $^{\circ}$K and by a factor of 54 at 500 $^{\circ}$K. At 300 $^{\circ}$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 $2 \times 10^{-13}\sqrt{T}$ 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^{1}0) to the lower radiating state (00^{0}0) 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^{0}0 and 01^{1}0. 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

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

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

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 $^{\circ}K$ 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.
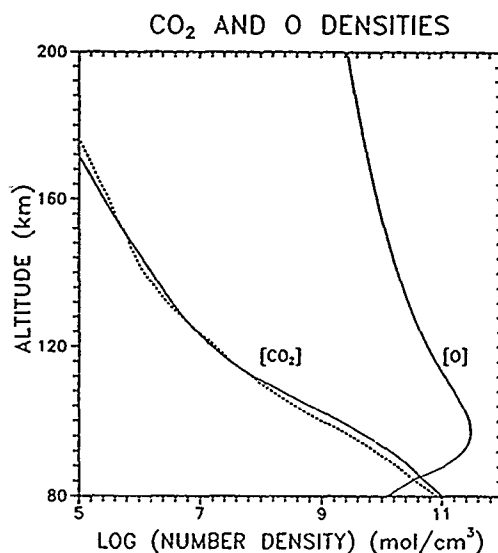

CO_2 AND O DENSITIES

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.

SPIRE BAND RADIANCE, 13-16.5 μm

A = 1.5
A = 3.0
A = 4.0
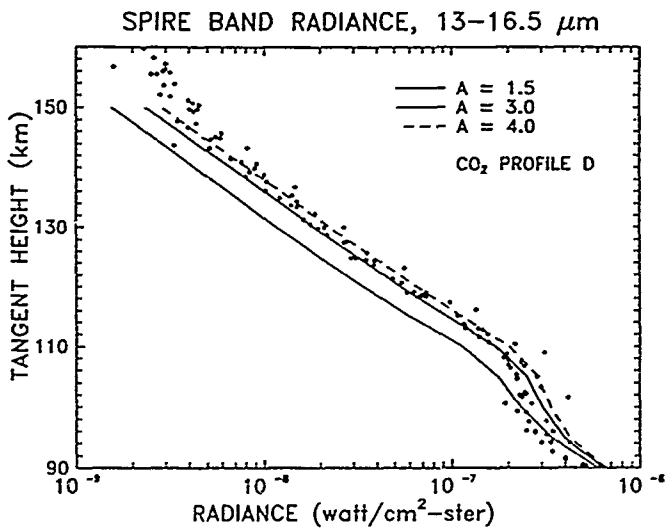
CO₂ PROFILE D

RADIANCE (watt/cm²-ster)

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.
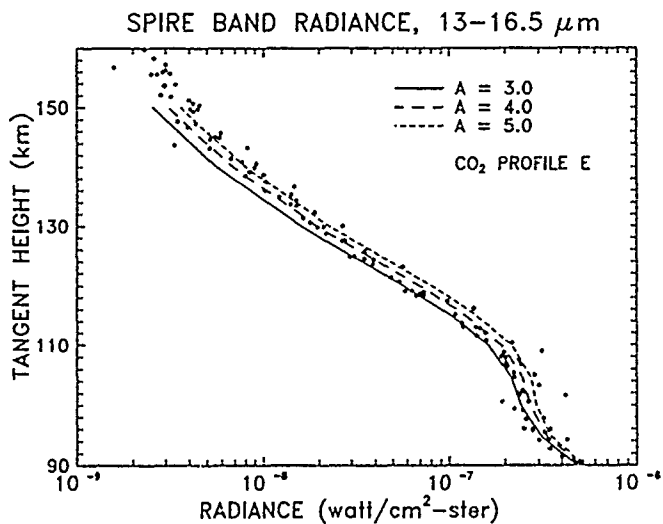
SPIRE BAND RADIANCE, 13-16.5 μm

A = 3.0
A = 4.0
A = 5.0

CO₂ PROFILE E

RADIANCE (watt/cm²-ster)

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.
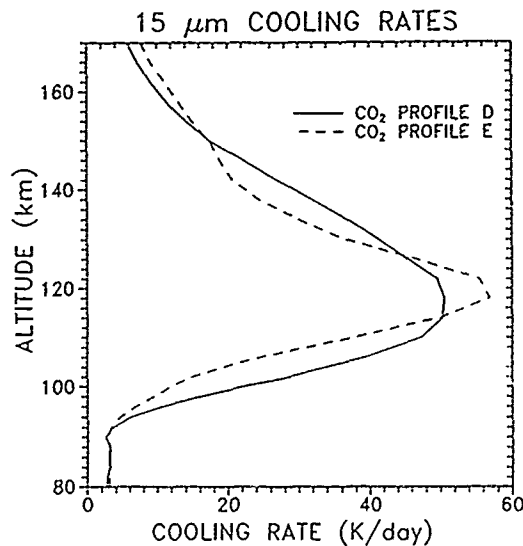
15 μm COOLING RATES

CO₂ PROFILE D
CO₂ PROFILE E

COOLING RATE (K/day)

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.

References

Allen, D.C., T. Scragg, and C.J.S.M. Simpson, Low temperature fluorescence studies of the deactivation of the bend-stretch manifold of CO_2, *Chem. Phys. 51*, 279-298, 1980.

Anderson, G.P., S.A. Clough, F.X. Kneizys, J.H. Chetwynd, and E.P. Shettle, AFGL Atmospheric Constituent Profiles (0-120 km), *Rep. AFGL-TR-86-0110, ADA 175173*, Geophysics Lab., Bedford, Mass., 1986.

Bougher, S.W., and R.E. Dickinson, Mars mesosphere and thermosphere, 1, global mean heat budget and thermal structure, *J. Geophys. Res. 93*, 7325-7337, 1988.

Beer, R., C.B. Farmer, M.R. Gunson, and R. Zander, Observational evidence for anomalous CO and CO_2 depletion above 80 km in the Earth's atmosphere, *Proc. Atmos. Spect. Applic. Workshop, 1-3 Sept 1987* (J. Ballard, ed.) RAL-88-009.

Chamberlain, J.W., and D.M. Hunten, *Theory of Planetary Atmospheres, An Introduction to Their Physics and Chemistry*, 2nd ed., Academic Press, N.Y., 1987.

Dickinson, R.E., Infrared radiative cooling in the mesosphere and lower thermosphere, *J. Atmos. Terr. Phys. 46*, 995-1008, 1984.

Dickinson, R.E., and S.W. Bougher, Venus mesosphere and thermosphere 1. Heat budget and thermal structure, *J. Geophys. Res. 91*, 70-80, 1986.

Dickinson, R.E., R.G. Roble, and S.W. Bougher, Radiative cooling in the NLTE region of the mesosphere and lower thermosphere—global energy balance, *Adv. Space Res. 7*, (10)5-(10)15, 1987.

Fox, J.L., Heating efficiencies in the thermosphere of Venus reconsidered, *Planet. Space Sci. 36*, 37-46, 1988.

Fox, J.L., and S.W. Bougher, Structure, luminosity, and dynamics of the Venus thermosphere, *Space Sci. Rev.*, in press, 1990.

Girard, A., J. Besson, D. Brard, J. Laurent, M.-P. Lemaitre, C. Lippens, C. Muller, J. Vercheval, and M. Ackerman, Global results of grille spectrometer experiment on board Spacelab 1, *Planet. Space Sci. 36*, 291-300, 1988.

Gordiets, B.F., Yu.N. Kulikov, K.N. Markov, and M.Ya. Marov, Numerical modeling of the thermospheric heat budget, *J. Geophys. Res. 87*, 4504-4514, 1982.

Hedin, A.E., H.B. Niemann, W.T. Kasprzak, and A. Seiff, Global empirical model of the Venus thermosphere, *J. Geophys. Res. 88*, 73-83, 1983.

Hedin, A.E., MSIS-86 thermospheric model, *J. Geophys. Res. 92*, 4649-4662, 1987.

Hedin, A.E., Atomic oxygen modeling in the upper thermosphere, *Planet. Space Sci. 36*, 907-920, 1988.

Hollenbach, D.J., S.S. Prasad, and R.C. Whitten, The thermal structure of the dayside upper atmosphere of Venus above 125 km, *Icarus 64*, 205-220, 1985.

Keating, G.M., and S.W. Bougher, Venus thermospheric response to short-term solar variations, *Adv. Space Res.*, in press, 1990.

Kumer, J.B., and T.C. James, SPIRE data evaluation and nuclear IR fluorescence processes, *Rep. DNA-6237F*, Defense Nuclear Agency, Washington, D.C., 1982.

Lunt, S.L., C.T. Wickham-Jones, and C.J.S.M. Simpson, Rate constants for the deactivation of the 15 μm band of carbon dioxide by the collision partners CH_3F, CO_2, N_2, Ar, and Kr over the temperature range 300 to 150 K, *Chem. Phys. Lett. 115*, 60-64, 1985.

Nier, A.O., and M.B. McElroy, Composition and structure of Mars' upper atmosphere: results from the neutral mass spectrometers on Viking 1 and 2, *J. Geophys. Res. 82*, 4341-4349, 1977.

Offermann, D., and K.U. Grossmann, Thermospheric density and composition as determined by a mass spectrometer with cryo ion source, *J. Geophys. Res., 78*, 8296-8304, 1973.

Offermann, D., V. Friedrich, P. Ross, and U. Von Zahn, Neutral gas composition measurements between 80 and 120 km, *Planet. Space Sci. 29*, 747-764, 1981.

Roble, R.G., E.C. Ridley, and R.E. Dickinson, On the mean structure of the thermosphere, *J. Geophys. Res. 92*, 8745-8758, 1987.

Sharma, R.D., and R.M. Nadile, Carbon dioxide (ν_2) radiance results using a new nonequilibrium model, paper presented at 19th Aerospace Sciences Meeting, Am. Inst. of Aeronaut. and Astronaut., St. Louis, Mo., Jan 12-15, 1981.

Sharma, R.D., Infrared airglow, in *Progress in Atmospheric Physics*, edited by R. Rodrigo and M. Lopez-Puertas, pp. 177-186, Kluwer Academic Publishers, Boston, Mass., 1988.

Simpson, C.J.S.M., P.D. Gait, and J.M. Simmie, The vibrational deactivation of the bending mode of CO_2 by O_2 and by N_2, *Chem. Phys. Lett. 47*, 133-136, 1977.

Stair, Jr., A.T., R.D. Sharma, R.M. Nadile, D.J. Baker, and W.F. Grieder, Observations of limb radiance with cryogenic spectral infrared rocket experiment, *J. Geophys. Res. 90*, 9763-9775, 1985.

Taine, J., and F. Lepoutre. A photoacoustic study of the collisional deactivation of the first vibrational levels of CO_2 by N_2 and CO, *Chem. Phys. Lett. 65*, 554-558, 1979.

Taine, J., F. Lepoutre, and G. Louis, A photoacoustic study of the collisional deactivation of CO_2 by N_2, CO, and O_2 between 160 and 375 K, *Chem. Phys. Lett. 58*, 611-615, 1978.

Taylor, R.L., Energy transfer processes in the stratosphere, *Can. J. Chem. 52*, 1436-1451, 1974.

Trinks, H., and K.H. Fricke, Carbon dioxide concentrations in the lower thermosphere, *J. Geophys. Res. 83*, 3883-3886, 1978.

Trinks, H., D. Offermann, U. Von Zahn, and C. Steinhauer, Neutral composition measurements between 90- and 220-km altitude by rocket-borne mass spectrometer, *J. Geophys. Res. 83*, 2169-2176, 1978.

Vercheval, J., C. Lippens, C. Muller, M. Ackerman, M.-P. Lemaitre, J. Besson, A. Girard, and J. Laurent, CO_2 and CO vertical distribution in the middle atmosphere and lower thermosphere deduced from infrared spectra, *Ann. Geophysicae 4*, 161-164, 1986.

Wintersteiner, P.P., R.D. Sharma, J.R. Winick, R.H. Picard, and R.A. Joseph (abstract), *EOS Trans. AGU 69*, 1346, 1988.

Wintersteiner, P.P., and R.D. Sharma, Update of an Efficient Code (NLTE) to Calculate Emission and Transmission of Radiation Through Non-Equilibrium Atmospheres, *AFGL-TR-85-0240, ADA 172556*, Geophysics Lab., Bedford, Mass., 1985.

R. D. Sharma, Optical and Infrared Technology Division, Geophysics Laboratory, Hanscom AFB, MA, 01731.

P. P. Wintersteiner, ARCON Corp., 260 Bear Hill Rd., Waltham, MA, 02154.