Atmospheric
Chemistry
and Physics

Technical Note: On the possibly missing mechanism of 15 µm emission in the mesosphere–lower thermosphere (MLT)

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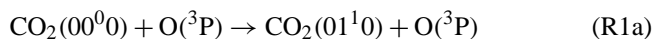*Correspondence to:* R. D. Sharma (rsharma.win@gmail.com)

Abstract. Accurate knowledge of the rate as well as the mechanism of excitation of the bending mode of CO_2 is necessary for reliable modeling of the mesosphere–lower thermosphere (MLT) region of the atmosphere. Assuming the excitation mechanism to be thermal collisions with atomic oxygen, the rate coefficient derived from the observed 15 µm emission by space-based experiments ($k_{ATM} = 6.0 \times 10^{-12} \, cm^3 s^{-1}$) differs from the laboratory measurements ($k_{LAB} = (1.5 - 2.5) \times 10^{-12} \, cm^3 s^{-1}$) by a factor of 2–4. The general circulation models (GCMs) of Earth, Venus, and Mars have chosen to use a median value of $k_{GCM} = 3.0 \times 10^{-12} \, cm^3 s^{-1}$ for this rate coefficient. As a first step to resolve the discrepancies between the three rate coefficients, we attempt to find the source of disagreement between the first two. It is pointed out that a large magnitude of the difference between these two rate coefficients ($k_x \equiv k_{ATM} - k_{LAB}$) requires that the unknown mechanism involve one or both major species: N_2, O. Because of the rapidly decreasing volume mixing ratio (VMR) of CO_2 with altitude, the exciting partner must be long lived and transfer energy efficiently. It is shown that thermal collisions with N_2, mediated by a near-resonant rotation-to-vibration (RV) energy transfer process, while giving a reasonable rate coefficient k_{VR} for de-excitation of the bending mode of CO_2, lead to vibration-to-translation k_{VT} rate coefficients in the terrestrial atmosphere that are 1–2 orders of magnitude larger than those observed in the laboratory. It is pointed out that the efficient near-resonant rotation-to-vibration (RV) energy transfer process has a chance of being the unknown mechanism if very high rotational levels of N_2, produced by the reaction of N and NO and other collisional processes, have a super-thermal population and are long lived. Since atomic oxygen plays a critical role in the mechanisms discussed here, it suggested that its

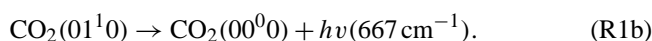density be determined experimentally by ground- and space-based Raman lidars proposed earlier.

1 Introduction

The 15 µm emission from CO_2 is the dominant cooling mechanism in the MLT region (Gordiets et al., 1982; Dickinson, 1984; Sharma and Wintersteiner, 1990; Wintersteiner et al., 1992; López-Puertas et al., 1992; Sharma and Roble, 2002). The magnitude of this cooling impacts both the temperature and height of the terrestrial mesopause (Bougher et al., 1994). This process is also important in the Martian and Venusian atmospheres (Bougher et al., 1999), especially the latter, where it acts as a thermostat during the long day (243 times the length of terrestrial day). The 15 µm emission from CO_2 has been used by a number of satellites (Offermann et al., 1999; Russell et al., 1999; Fischer et al., 2008) to retrieve atmospheric temperature as a function of altitude. Finding the mechanism leading to this emission is therefore very important.

Translational energy (heat) is collisionally converted into vibrational energy of the bending mode of CO_2. A fraction of the resulting vibrational energy is radiated away to space, cooling the atmosphere. The dominant mechanism for this conversion is believed to be the collisions between CO_2 and O,

$$CO_2(00^00) + O(^3P) \rightarrow CO_2(01^10) + O(^3P) \qquad \text{(R1a)}$$

and

$$CO_2(01^10) \rightarrow CO_2(00^00) + h\nu(667 \, cm^{-1}). \qquad \text{(R1b)}$$

This process is endothermic by the energy of the emitted photon, $667\,cm^{-1}$ ($\sim 15\,\mu m$). In the chemical literature, the rate coefficients of the reactions are given in the exothermic direction (reverse of Reaction 1a), and we will follow that convention. The room temperature value of the rate coefficient k_{ATM} for the exothermic process derived by modeling the $15\,\mu m$ emission, observed by the Spectral Infrared Rocket Experiment (SPIRE) (Stair et al., 1985) from the MLT region of the atmosphere, is $5 \times 10^{-13}\,cm^3\,s^{-1}$ (Sharma and Nadile, 1981), $5.2 \times 10^{-12}\,cm^3\,s^{-1}$ (Stair et al., 1985), $3.5 \times 10^{-12}\,cm^3\,s^{-1}$ (Sharma, 1987), and $(3-9) \times 10^{-12}\,cm^3\,s^{-1}$ (Sharma and Wintersteiner, 1990). These studies gave values of k_{ATM} that are 1–2 orders of magnitude greater than values recommend earlier (Crutzen, 1970; Taylor, 1974). Later analyses of space-based observations have given values around 6×10^{-12} ($cm^3\,s^{-1}$) (Wintersteiner et al., 1992; López-Puertas et al., 1992; Ratkowski et al., 1994; Gusev et al., 2006; Feofilov et al., 2012, and references therein), except for the Vollmann and Grossmann (1997) study giving a value of 1.5×10^{-12} ($cm^3\,s^{-1}$). The study of Feofilov et al. (2012) determined the rate coefficient by coincidental SABER/TIMED and Fort Collins sodium lidar observations in the MLT region and arrived at values of $(5.5 \pm 1.1) \times 10^{-12}\,cm^3\,s^{-1}$ at 90 km altitude and $(7.9 \pm 1.2) \times 10^{-12}\,cm^3\,s^{-1}$ at 105 km, with an average value of $(k_{ATM} = 6.5 \pm 1.5) \times 10^{-12}\,cm^3\,s^{-1}$. The study of López-Puertas et al. (1992) "suggests a value of between 3 and $6 \times 10^{-12}\,cm^3\,s^{-1}$ at 300 K" and temperature "independent or negative temperature dependence". This study derives the values for all input parameters from ATMOS/Spacelab 3 observations (Farmer et al., 1987; Rinsland et al., 1992), except the VMR of atomic oxygen, which is taken from atmospheric models.

The laboratory measurements (Shved et al., 1991; Pollock et al., 1993; Khvorostovskaya et al., 2002; Castle et al., 2006, 2012) and theoretical calculations (de Lara-Castells et al., 2006, 2007) give room temperature values of $k_{LAB} \approx (1.5-2.5) \times 10^{-12}$ ($cm^3\,s^{-1}$). The values of k_{VT} determined by modeling $15\,\mu m$ emission from the MLT region, termed k_{ATM}, are thus larger than the calculated and measured values by a factor of about 4. Castle et al. (2012) have measured the deactivation of $CO_2(v_2)$ by $O(^3P)$ in the 142–490 K temperature range, obtaining values of the rate coefficient $k_{LAB} = (2.5 \pm 0.4) \times 10^{-12}\,cm^3\,s^{-1}$ at 183 K and $(2.4 \pm 0.4) \times 10^{-12}\,cm^3\,s^{-1}$ at 206 K. The unexplained rate coefficient $k_x(v_2)$ is $(5.6 \pm 1.1 - 2.5 \pm 0.4) \times 10^{-12} = (3.1 \pm 1.5) \times 10^{-12}\,cm^3\,s^{-1}$ at 90 km altitude ($T \approx 183\,K$) and is $(7.9 \pm 1.2 - 2.4 \pm 0.4) \times 10^{-12} = (5.5 \pm 1.6) \times 10^{-12}\,cm^3\,s^{-1}$ at 105 km altitude (Table 1b). $k_x(v_2)$ increases by a factor of 1.8 in going from 90 km altitude to 105 km altitude ($\approx 206\,K$), showing a steep variation with altitude. Using the average of the value of k_{ATM} 3 and $6 \times 10^{-12}\,cm^3\,s^{-1}$, $4.5 \times 10^{-12}\,cm^3\,s^{-1}$, suggested by López-Puertas et al. (1992), and $k_{LAB} = 2.5 \times 10^{-12}\,cm^3\,s^{-1}$, we get $k_x = 2.0 \times 10^{-12}\,cm^3\,s^{-1}$, a smaller value independent of temperature (altitude). It should be noted that the

contribution to the rate coefficient k_{ATM} by unknown mechanism k_x nearly equals (López-Puertas et al., 1992) or is greater (Feofilov et al., 2012) than k_{LAB}, the contribution by the major constituent atomic oxygen. As pointed out by Feofilov (2014), the GCM (general circulation models) use of a value of $k_{GCM} = 3.0 \times 10^{-12}\,cm^3\,s^{-1}$ for this rate coefficient (Bougher et al., 1999) further complicates the problem. To resolve this difficult problem, we break it into pieces and attempt to find the cause of discrepancy between k_{ATM} and k_{LAB}.

To resolve the discrepancy between k_{ATM} and k_{LAB}, Feofilov et al. (2012) postulate that nonthermal, or "hot", oxygen atoms, produced in the MLT region by photolysis of O_2 and dissociative recombination of O_2^+, etc., may serve as an additional source of $CO_2(v_2)$ level excitation. These authors have derived CO_2 volume mixing ratio (VMR) parts per million by volume (ppmv) in the MLT region for the time of their experiment from atmospheric models as well as space-based observations. The average VMR, according to the MLW atmosphere, is about 268 ppmv at 90 km altitude and about 105 ppmv at 105 km altitude, in general agreement with the values given by Rinsland et al. (1992). This means that for every collision a "hot" oxygen atom undergoes with CO_2, it must undergo ($10^6/268 =$)3731 collisions at 90 km altitude and ($10^6/105 =$)9524 collisions at 105 km altitude with other atmospheric constituents, mostly with N_2, O_2 and O. Solution of the time-dependent Boltzmann equation with realistic potential functions (Dothe et al., 1997) has shown that a 1 eV "hot" atom loses most of its energy in a few collisions. The chance of a "hot" atom colliding with CO_2 is therefore virtually nil. However, since CO_2 is the dominant constituent in the Martian and Venusion atmospheres, "hot" O atoms may play a significant role in exciting its vibrations on these planets. In the terrestrial atmosphere, another reservoir of energy that either takes energy from various nonthermal energy sources, e.g., "hot" O atoms, and that may or may not be in local thermodynamic equilibrium, but one that readily transfers energy preferentially to the bending mode of CO_2 must be found to explain large k_x. The situation is similar to that of elevated $4.3\,\mu m$ (v_3 mode) CO_2 emissions from the hydroxyl layer in the nocturnal mesosphere (Kumer et al., 1978; López-Puertas et al., 2004). Highly vibrationally excited OH, produced by the reaction of $H + O_3$, because of its short lifetime can only transfer a very small amount of energy directly to trace species CO_2, even though transfer of vibrational energy from higher levels ($v = 8$ and 9) of OH to the v_3 mode of CO_2 is a fast near-resonant process (Burtt and Sharma, 2008b). The vibrational energy from higher levels ($v = 8$ and 9) of OH is instead transferred to N_2 by a fast near-resonant process (Burtt and Sharma, 2008a). The longer-lived and super-thermal vibrationally excited N_2 transfers its energy, again by a fast near-resonant process (Sharma and Brau, 1967, 1969), to the v_3 mode of CO_2, the latter radiating around $4.3\,\mu m$. The longer-lived $N_2(v = 1)$

molecule acts as a reservoir that takes energy from OH and stores it until it is preferentially released to CO_2.

2 Hypothesis

We advance the hypothesis that rotational degrees of freedom of N_2 and O_2 are the reservoirs that transfer their energy efficiently to the v_2 mode of CO_2. High rotational levels of these reservoirs by a near-resonant rotation-to-vibration energy transfer process are responsible for efficiently exciting the bending (v_2) mode of CO_2 leading to 15 μm emission. These rotational levels may be thermal or long-lived nonthermal.

3 Test of the hypothesis

3.1 Thermal rotational levels

Since the N_2 density at the altitudes under consideration is much greater than the O_2 density, we provide a justification for the deactivation of $CO_2(01^10)$ by N_2. The reaction

$$CO_2(01^10) + N_2(J) \rightarrow CO_2(00^00) + N_2(J+8) + \Delta E \quad (R2)$$
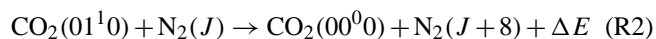
is exothermic by 46 and 14 cm^{-1} for $J = 15$ and 16 and endothermic by 17 and 49 cm^{-1} for $J = 17$ and 18. The CO_2 molecule, in the dipole-hexadecapole moment and quadrupole–hexadecapole moment interactions involved undergoes $\Delta J = \pm 3, \pm 2, \pm 1, 0$ in the process. Since CO_2 has a much smaller rotational constant (≈ 0.39 cm^{-1}) than N_2 (≈ 1.99 cm^{-1}), we, for the rough estimate, ignore the contributions of its rotational transitions to the energy transfer process. The near-resonant processes, mediated by long-range multipole and dispersion interactions, transfer a small amount of energy from internal degrees of freedom (vibration and rotation) to translation, and can therefore have a much larger cross section. On the other hand, processes that require transfer of a large amount of energy from internal (vibration and rotation) degrees of freedom to translation and can be mediated only by short-range repulsive forces tend to have a smaller cross section. This is the rationale for selecting $\Delta J = 8$ transitions, since they are both near-resonant and can be mediated by long-range forces. At 183 K, a temperature relevant to the MLS atmosphere (Table 1b), at about 90 km altitude, about 2.4 % of the N_2 molecules reside in one of these four rotational levels. The density of N_2 in these four thermalized rotational levels is $(0.0241/0.018 =)1.34$ times that of atomic oxygen. The unexplained rate coefficient $k_x(v_2)$ at 90 km altitude for pumping of the v_2 mode of CO_2 is $(3.1 \pm 1.5) \times 10^{-12}$ cm^{3}s^{-1}. The sum of the rate coefficients of Reaction (R2) at 168 K for all four rotational levels $k_{VR}(N_2)$ has to be nearly equal to or greater than $(3.1 \pm 1.5) \times 10^{-12}/1.34 = (2.32 \pm 1.1) \times 10^{-12}$ cm^{3}s^{-1} to make Reaction (R2) the dominant mechanism for pumping of the v_2 mode of CO_2. Since only 2.4 % of the N_2

molecules participate in the RV energy transfer process, the rate coefficient for deactivation of $CO_2(v_2)$ by N_2 would be $k_{VT}(N_2) = ((2.32 \pm 1.1) \times 0.024) \times 10^{-12} = (5.6 \pm 2.6) \times 10^{-14}$. A larger calculated rate coefficient k_{N_2} would not be a problem, since the v_2 mode of CO_2 at least up to 90 km altitude is in local thermodynamic equilibrium (LTE); i.e., its vibrational temperature is nearly the same as the translational temperature (Feofilov et al., 2012; López-Puertas et al., 1992; Stair et al., 1985). Tables 1a–d, using the atmospheres, provided by Feofilov and López-Puertas, give the rate coefficients $k_{VT}(N_2)$, the fifth column, and $k_{VR}(N_2)$, the last column, required by k_x given by these atmospheres. The rate coefficient $k_{VT}(N_2)$ for the deactivation of the bending mode of CO_2 by N_2 at low temperatures has been measured at room temperature by Merrill and Amme (1969) using ultrasonic velocity dispersion measurements and by Cannemeyer and De Vries (1974) using an optic–acoustic effect. Taine et al. (1978, 1979), by the photoacoustic method, and Allen et al. (1980), by the laser fluorescence technique, have measured $k_{VT}(N_2)$ at low temperatures. These studies are in general agreement with that of Allen et al. (1980) giving $k_{VT}(N_2)$ equal to 1.4×10^{-15} cm^{3}s^{-1} at 170 K and 3.7×10^{-15} cm^{3}s^{-1} 295 K about 1 order of magnitude smaller at lower temperature and 2 orders magnitude smaller at higher temperature than the values given in Tables 1a–d. Clearly, another mechanism is needed to explain the large observed values of $k_x \equiv k_{ATM} - k_{LAB}$. It has already been noted that, since k_x is almost equal to (Tables 1c and d) or greater (Tables 1a and b) than k_{LAB}, it must involve a major species with a large rate coefficient.

3.2 Nonthermal rotational levels

Sharma (1971) has calculated the probability per collision of the reaction

$$CO_2(01^10) + H_2O \rightarrow CO_2(00^00) + H_2O, \quad (R3)$$

a much studied process because of its importance in CO_2 lasers, assuming a vibration-to-rotation (VR) energy transfer (ET) mechanism mediated by long-range multipolar interactions. In spite of a large scatter in the experimental data, a situation typical of low-temperature experiments involving water vapor, the agreement is quite good. The calculated probability per collision is 0.06 at 200 K and 0.08 at 300 K. The rate coefficients (σv), assuming a gas kinetic rate of 2×10^{-10} cm^3 s^{-1} at 200 K and 2.5×10^{-10} cm^3 s^{-1} at 300 K, are 1.2×10^{-11} and 2.0×10^{-11} cm^3 s^{-1} at 200 and 300 K, respectively.

Allen et al. (1980) have measured rate coefficients for the deactivation of the bend-stretch mode of CO_2 by H_2 in the 170–295 K temperature range, obtaining values of 7.5×10^{-12} and 5.0×10^{-12} cm^3 s^{-1} at 170 and 295 K, respectively, the probability of energy transfer per collision P at the two temperatures being 1.4×10^{-2} and 7.4×10^{-3}. The inverse temperature dependence of this rate coefficient

Table 1. Rate coefficient for deactivation of $CO_2(v_2)$ by thermal N_2, $k_{VT}(N_2)$, required if collisions with thermal N are the missing source of 15 µm emission as function of altitude for different model atmospheres. (a) MLW atmosphere (A. G. Feofilov, 19 October 2014), (b) MLS atmosphere (A. G. Feofilov, 19 October 2014), (c) polar summer SABER model atmosphere (López-Puertas, 11 November 2014), and (d) polar winter SABER model atmosphere (López-Puertas, 11 November 2014).

	Altitude (km)	Temperature (K)	k_x	(O VMR)/(N$_2$ VMR)	$k_{VT}(N_2)$	N$_2$P4(J)	$k_{VT}(N_2)$
(a)							
	91	169	3.4	0.023	0.0782	0.0183	4.27
	93	174	4.1	0.029	0.1189	0.0206	5.77
	96	185	4.7	0.043	0.2021	0.0249	8.12
	99	199	5.0	0.056	0.280	0.0314	8.92
	102	213	5.2	0.089	0.463	0.0381	12.1
	105	227	5.4	0.129	0.697	0.0451	15.4
(b)							
	90	183	3.1	0.018	0.0558	0.0241	2.32
	93	179	4.1	0.028	0.1148	0.0223	5.15
	96	178	4.7	0.05	0.235	0.0218	10.8
	99	182	5.1	0.079	0.4029	0.0237	17.0
	102	191	5.2	0.156	0.8112	0.0277	29.3
	105	206	5.4	0.219	1.1826	0.0372	31.8
(c)							
	95	179.7	2.0	0.0198	0.0396	0.02264	1.75
	98	183.7	2.0	0.0358	0.0716	0.02438	2.97
	101	194.5	2.0	0.0591	0.1182	0.02927	4.04
	104	214.6	2.0	0.0920	0.184	0.03897	4.72
	107	254.8	2.0	0.130	0.260	0.05928	4.39
	110	304.4	2.0	0.163	0.326	0.08339	3.91
(d)							
	95	179.6	2.0	0.0125	0.025	0.02264	1.10
	98	239.7	2.0	0.021	0.042	0.05162	0.814
	101	296.0	2.0	0.031	0.062	0.07949	0.780
	104	346.8	2.0	0.041	0.082	0.1016	0.807
	107	380.3	2.0	0.047	0.094	0.1142	0.823
	110	395.2	2.0	0.054	0.108	0.1192	0.906

Rate coefficients are in units of $cm^3 s^{-1} \times 10^{12}$.
$k_x = k_{ATM} - k_{LAB}$. k_{ATM} provided by A. G. Feofilov (3 November 2014). k_{LAB} is taken as equal to $2.5 \times 10^{12} \, cm^3 \, s^{-1}$ throughout, based on the work of Castle et al. (2012).
$k_{VT}(N_2)$ is the $N_2 - CO_2(v_2)$ VT rate coefficient needed to explain k_x.
N$_2$P4(J) is the fraction of N_2 molecules in the four rotational levels 15–18.
$k_{VR}(N_2)$ is the $N_2 - CO_2(v_2)$ VR rate coefficient needed to explain k_x.
$k_x = k_{ATM} - k_{LAB}$; k_{ATM} provided by A. G. Feofilov (3 November 2014). k_{LAB} is taken as equal to $2.5 \times 10^{12} \, cm^3 \, s^{-1}$ throughout, based on Castle et al. (2012).
$k_{ATM} = 4.5 \times 10^{-12} \, cm^3 \, s^{-1}$ is the average of $(3 - 6) \times 10^{-12} \, cm^3 \, s^{-1}$ given by López-Puertas et al. (1992).

is at odds with the Landau–Teller TV energy transfer mechanism and very much in accord with the near-resonant energy transfer mechanism (Sharma and Brau, 1967, 1969). Sharma (1969) has calculated the deactivation of $CO_2(v_2)$ by H_2 assuming a near-resonant VR energy transfer mechanism mediated by dipole–quadrupole interaction,

$$CO_2(01^10) + H_2(v = 0, J = 1) \rightarrow CO_2(00^00) \quad (R4)$$
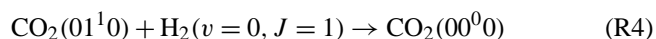
obtaining inverse temperature dependence with P (300 K) $\approx$ 4×10^{-3} and good agreement with the then available data, but smaller than the value measured by Allen et al. (1980) by a factor of about 2.

The VR energy transfer processes are seen to be capable of giving rate coefficients of a desired magnitude. The only molecule with large and nearly constant VMR with an altitude capable of collisionally converting the vibrational energy of $CO_2(01^10)$ into its rotational energy is N_2.

Rotationally super-thermal N_2 may be produced by collisions of fast O atoms with N_2. Sharma and Sindoni (1993) have calculated the differential cross section of Ar-CsF colliding with 1.0 initial relative translational energy as a function of the laboratory recoil velocity of CsF, obtaining excellent agreement for all eight laboratory scattering angles for which the data were available. The calculation exhibits a rich rotational structure showing primary and supernumerary rainbows, with rotational levels of CsF as high as $J = 194$ populated. There is no reason why correspondingly high rotational levels of N_2 may not be populated in collisions with fast O atoms.

Duff and Sharma (1996, 1997) have calculated the rate coefficient of the reaction of N with NO,

$$N + NO \rightarrow N_2 + O + 3.25\,eV, \tag{R5}$$

in the 100–1000 K temperature, obtaining excellent agreement with the available experimental data and conforming to JPL recommendations (Sander et al., 2011). The calculation (Duff and Sharma, 1997) shows that the product N_2 is produced in excited vibrational and rotational states; vibrational levels 2–7 are each populated with a probability of about 0.1, with rotational levels of vibrational states 1–4 peaking around $J = 45$, while those of vibrational states 5–8 peaked around $J = 40$. The VR energy transfer process

$$CO_2(01^10) + N_2(v = xx, J) \rightarrow CO_2(00^00)$$
$$+ N_2(v = xx, J + 4) + \Delta E \tag{R6}$$
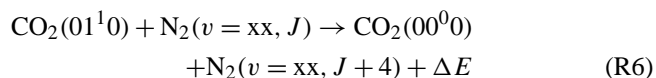
is near-resonant, with $|\Delta E| \leq 50\,cm^{-1}$ for seven rotational levels 36–42. This process has the potential to be the sought-after mechanism, provided rotational levels relax in small steps ($\Delta J = -2, \Delta E \approx 230\,cm^{-1}$) with a small rate coefficient. The calculation would proceed in the manner of Sharma and Kern (1971), who showed that the greater rate of deactivation of vibrationally excited CO by para-hydrogen over ortho-hydrogen is due to the near-resonant VR process mediated by multipolar interactions

$$CO(v = 1) + H_2(v = 0, J = 2) \rightarrow CO(v = 0)$$
$$+ H_2(v = 0, J = 6) + 88\,cm^{-1}. \tag{R7}$$
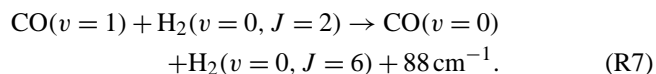
4 Conclusions

A large value of k_x requires the rate coefficient of the unknown mechanism to be equal to $k_x \times$ (M VMR)/(O VMR), where M is the species participating in the unknown mechanism. While k_x may stay constant or increase by a factor of less than 2, the O atom VMR increases by about 1 order of magnitude, going from 90 to 105 km in altitude. The only species that stands a chance of meeting these stringent requirements is N_2; its VMR, while not increasing, stays nearly constant at about 0.78. It is shown that the $CO_2(v_2)$–N_2 near-resonant VR rate coefficients could be large enough to meet

the requirements. In the thermal atmosphere, the VR processes lead to VT rate coefficients that are 1–2 orders of magnitude too large. Rotationally super-thermal N_2, produced by collisions of fast O atoms with N_2 or by the N + NO reaction or any other mechanism, hold out hope if these rotational levels relax in small steps ($\Delta J = -2, \Delta E \approx 230\,cm^{-1}$) with a small rate coefficient.

The 15 μm (bending mode v_2) emission from CO_2 is also an important cooling mechanism in the atmospheres of Venus and Mars (Bougher et al., 1999), especially the former, where it acts as a thermostat during the long day (243 times the length of the terrestrial day). The atmospheres of Venus and Mars are similar ($\sim 95\,\%\ CO_2$, a few percent of N_2) and, in these atmospheres, direct excitation of CO_2 vibrations by fast O atoms may be an important cooling mechanism.

The density of atomic oxygen plays very important role in cooling planetary atmospheres. Recently published values of atomic oxygen density (Kaufmann et al., 2014) derived from nighttime limb measurements of atomic oxygen green line intensity in the mesopause region, by the SCIA-MACHY instrument on the European Environmental Satellite, are "at least 30 % lower than atomic oxygen abundances obtained from SABER" instrument on the TIMED satellite. Perhaps it is time that atomic oxygen density is measured using the ground-based (Sharma and Dao, 2006) and space-based (Sharma and Dao, 2005) Raman lidars proposed earlier.

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