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Technical Note: A new mechanism of 15 μm emission in the mesosphere-lower thermosphere (MLT)

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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 differ from the laboratory measurements by a factor of 2–4. It is proposed that thermal collisions with N_2, mediated by a near-resonant rotation to vibration energy transfer process, excite bending mode of CO_2 by transferring energy from high rotational levels of thermal N_2. Analogy with the excitation of the bending mode of CO_2 by H_2O, a process important in CO_2 lasers, mediated by a near-resonant rotation-to vibration energy transfer process lends credibility to the hypothesis which has yet to be tested by direct calculations.

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; 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

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space cooling the atmosphere. The dominant mechanism for this conversion is believed to be the collisions between CO_2 and O,

$$CO_2(0^00) + O(^3P) \rightarrow CO_2(0^110) + O(^3P) - 667cm^{-1} \quad \text{(R1)}$$

This process is endothermic by the energy of the emitted photon, 667 cm^{-1} (~ 15 µm). In chemical literature, the rate coefficients of the reactions are given in the exothermic direction (reverse of Eq. 1) and we will follow that convention. The room temperature value of the rate coefficient k_O for the exothermic process derived by modeling the 15 µm emission, observed by Spectral Infrared Rocket Experiment (SPIRE) (Stair et al., 1985), from the MLT region of the atmosphere is 5×10^{-13} cm^3 s^{-1} (Sharma and Nadile, 1981), 5.2×10^{-12} cm^3 s^{-1} (Stair et al., 1985), 3.5×10^{-12} cm^3 s^{-1} (Sharma, 1987), $(3–9) \times 10^{-12}$ cm^3 s^{-1} (Sharma and Wintersteiner, 1990). These studies gave values of k_O 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; 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 this 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 $(6.5 \pm 1.5) \times 10^{-12}$ cm^3 s^{-1}.

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_{VT} near 1.5×10^{-12} (cm^3 s^{-1}). The values of k_{VT} determined by modeling 15 µm emission from the MLT region are thus larger than the calculated and measured values by a factor of about four. 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 $k_O(v_2)$ =

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$(2.5 \pm 0.4) \times 10^{-12}$ cm^3 s^{-1} at 168 K and $(1.9 \pm 0.3) \times 10^{-12}$ cm^3 s^{-1} at 272 K. Unexplained rate coefficient $k_u(v_2)$ is $(5.5 - 2.5 =) 3.0 \times 10^{-12}$ cm^3 s^{-1} at 90 km altitude ($T \approx 168$ K) and is $(7.9 - 1.9 =) 6.0 \times 10^{-12}$ cm^3 s^{-1} at 105 km altitude ($T \approx 272$ K). $k_u(v_2)$ increases by a factor of 2 in going from 90 km altitude (168 K) to 105 km altitude (272 K) showing a steep variation with altitude.

Feofilov et al. (2012) postulate that nonthermal 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 given by these authors is about 300 ppmv at 95 km altitude and about 140 ppmv at 105 km altitude. This means that for every collision a "hot" oxygen atom undergoes with CO_2, it must undergo $(10^6/300 =) 3333$ collisions at 95 km altitude and $(10^6/140 =) 7143$ 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. Another reservoir of energy that either takes energy from various energy sources or is in local thermodynamic equilibrium and one that readily transfers energy preferentially to bending mode of CO_2 must be found to explain the large k_{VT} rate coefficient. The situation is similar to that of elevated 4.3 µm (v_3 mode) CO_2 emission from the hydroxyl layer in the nocturnal mesosphere (Kumer et al., 1978; López-Puértas 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 specie CO_2 even though transfer of vibrational energy from higher levels ($v = 8$ and 9) of OH to 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 vibrationally excited N_2 transfers its energy, again by a fast

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near-resonant process (Sharma and Brau, 1969), to the v_3 mode of CO_2, the latter radiating around 4.3 µm. 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 the thermalized 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_2leading to 15 µm emission.

3 Justification of the Hypothesis

Since the N_2 density at the altitudes under consideration is much greater than O_2 density we provide justification for the deactivation of $CO_2(0^1 10)$ by N_2. The reaction

$$CO_2(0^1 10) + N_2(J) \rightarrow CO_2(0^0 00) + N_2(J + 8) + \Delta E \quad \text{(R2)}$$

is exothermic by 46 cm^{-1} and 14 cm^{-1} for $J = 15$ and 16 and endothermic by 17 cm^{-1} and 49 cm^{-1} for $J = 17$ and 18. Since the near-resonant processes require transfer of a small amount of energy from internal degrees of freedom (vibration and rotation) to translation and can be mediated by long-range multipole and dispersion interactions they can have much large cross section. On the other hand the processes that require transfer of 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 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 168 K, temperature relevant to about 90 km altitude, about 2.0 % of the N_2 molecules reside

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in one of these four rotational levels. The density of N_2 in these four thermalized rotational levels is $(0.02 \times 1.1 \times 10^{13} =) 2.2 \times 10^{11}\,cm^{-3}$ is about ten times that of atomic oxygen ($2.1 \times 10^{10}\,cm^{-3}$). The unexplained rate coefficient $k_u(v_2)$ at 90 km altitude for pumping of the v_2 mode of CO_2 is $3.0 \times 10^{-12}\,cm^3\,s^{-1}$. The sum of the rate coefficients of Reaction (R2) at 168 K for all four rotational levels has to be nearly equal or greater than $3 \times 10^{-13}\,cm^3\,s^{-1}$ to make Reaction (R2) the dominant mechanism for pumping the v_2 mode of CO_2. A larger calculated rate coefficient for Reaction (R2) would not be a problem since the v_2 mode of CO_2 at 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).

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

$$CO_2(0^110) + H_2O \rightarrow CO_2(0^00) + H_2O, \qquad \text{(R3)}$$

a much studied process because of its importance in CO_2 lasers, assuming a vibration-to-rotation (VR) energy transfer (ET) mechanisn. 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 $2 \times 10^{-10}\,cm^3\,s^{-1}$ at 200 K and $2.5 \times 10^{-10}\,cm^3\,s^{-1}$ at 300 K, are 1.2×10^{-11} and $2.0 \times 10^{-11}\,cm^3\,s^{-1}$ at 200 and 300 K, respectively. It is therefore eminently reasonable to assume that total rate coefficient of the four aforementioned rotational levels at 168 K (90 km altitude) may be quite large.

The population of the four levels of N_2 (J = 15–18) at 272 K (105 km altitude) is about 6.8 % of the N_2 population $(0.068 \times 2.1 \times 10^{12} =) 1.4 \times 10^{11}\,cm^{-3}$. This density is about the same as that of atomic oxygen ($1.6 \times 10^{11}\,cm^{-3}$). The unaccounted of rate coefficient at 105 km altitude for pumping of the v_2 mode of CO_2 is $k_u(v_2) = 6.0 \times 10^{-12}\,cm^3\,s^{-1}$. The sum of the rate coefficients of Reaction (R2) at 272 K for all four aforementioned rotational levels of N_2 has to be about $k_u(v_2) = 6.0 \times 10^{-12}\,cm^3\,s^{-1}$ to make these levels the dominant mechanism for pumping the v_2 mode of CO_2. This

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value of the rate coefficient $k_u(v_2)$ is smaller by a factor of 3 than that calculated for the deactivation of the v_2 mode of CO_2 by H_2O (Reaction R3) at 300 K making it a possible sought after mechanism. Since only 6.8 % of the N_2 molecules participate in the rotation-to-vibration (RV) energy transfer process a CO_2–N_2 RV rate coefficient at 272 K (105 km altitude) $k_u(v_2) \times 0.068 = 6.0 \times 10^{-12} \times 0.068 = 4.1 \times 10^{-13}$ cm^3 s^{-1}, about two orders of magnitude smaller than the CO_2–H_2O RV rate coefficient, would reconcile the experimental and field observations.

In a survey of vibrational relaxation data for processes important in CO_2–N_2 laser system Taylor and Bitterman (1969) report "two old sound dispersion experiments of limited extent", one (Wallman, 1934) giving a value of 2.0×10^{-14} cm^3 molecule^{-1} s^{-1} at 291 K, the second one (Metter, 1937) giving a value of 2.2×10^{-13} cm^3 molecule^{-1} s^{-1} at 273 K. The latter value of the rate coefficient, smaller only by a factor of 2 than the value needed, would resolve the problem at hand. Unfortunately, I was not able to locate either reference.

4 Conclusion

By analogy with the deactivation of the v_2 mode of CO_2 by H_2O, it is proposed that the mechanism for populating the v_2 mode of CO_2 in the MLT region is a rotation-to-vibration near-resonant energy transfer process. Translational temperature, like the atomic oxygen density, in the MLT region varies rapidly with altitude. It is this rapid increase in temperature and not the rapid increase in atomic oxygen density that explains rapid increase in unaccounted rate coefficient. It should be noted that while the density of N_2 decreases by a factor of about 5 in going from 90 to 105 km altitude the density of high rotational levels that can exchange energy with $CO_2(0^110)$ has decreased only by one-third. Much smaller decrease in the high rotational levels of N_2 is of course due to rapid increase of temperature with altitude. The hypothesis advanced here, although simple and straight forward, has yet to be tested by direct calculations. The calculations do not involve any non-equilibrium effects and therefore should not too difficult to

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carry out. In addition to the $CO_2(v_2)$–H_2O calculation (Sharma, 1971) mentioned earlier, similar calculations on deactivation of $CO_2(v_2)$ by H_2 and D_2 (Sharma, 1969) and deactivation of vibrationally excited CO by para-hydrogen (Sharma and Kern, 1971) were performed earlier.

The 15 µm (bending mode v_2) emission from CO_2 is also important cooling mechanism in the atmospheres of Venus and Mars, 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 (∼ 95 % CO_2, a few percent N_2) but very different from that of the Earth. Therefore, the proposed new mechanism for the excitation of the 15 µm (bending mode v_2) emission from CO_2 requires rate coefficients in the atmospheric models of Venusian and Martian that are different from those in the models of terrestrial atmosphere.

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