On the possibly missing 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 CO₂ 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 \( k_{\text{ATM}} = 6.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \) differ from the laboratory measurements \( k_{\text{LAB}} = (1.5 – 2.5) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \) by a factor of 2 – 4. The General Circulation Models (GCMs) of Earth, Venus, and Mars have chosen to use a median value of \( k_{\text{GCM}} = 3.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \) 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 large magnitude of the difference between these two rate coefficients \( k_x \equiv k_{\text{ATM}} – k_{\text{LAB}} \) requires that the unknown mechanism involve one or both major species; N₂, O. Because of the rapidly decreasing volume mixing ratio (vmr) of CO₂ with altitude the exciting partner must be long lived and transfer energy efficiently. It is shown that thermal collisions with N₂, mediated by a near-resonant rotation to vibration (RV) energy transfer process, while giving a reasonable rate coefficient \( k_{\text{VR}} \) for de-excitation of bending mode of CO₂ lead to vibration-to-translation \( k_{\text{VT}} \) 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 N₂, produced by the reaction of N and NO and other collisional processes, have 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.

**Key words:** 15 µm emission, CO₂, N₂, O, rotation, vibration, near-resonant energy transfer.

**Introduction.** The 15 µm emission from CO₂ is the dominant cooling mechanism in the MLT
region [Gordiets et al., 1982; Dickinson, 1984; Sharma and Wintersteiner, 1990; Wintersteiner et
al., 1992; López-Peurtas 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 CO₂ 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 CO₂. 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 CO₂ and O,

\[
\text{CO}_2(00^00) + \text{O}^{(3)}P \rightarrow \text{CO}_2(01^10) + \text{O}^{(3)}P \quad (1a)
\]

\[
\text{CO}_2(01^10) \rightarrow \text{CO}_2(00^00) + h\nu(667 \text{ cm}^{-1}) \quad (1b)
\]

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 equation 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 µm emission, observed by Spectral Infrared Rocket Experiment (SPIRE) \cite{Stair et al., 1985}, from the MLT region of the atmosphere is $5 \times 10^{-13}$ cm$^3$ s$^{-1}$ \cite{Sharma and Nadile, 1981}, $5.2 \times 10^{-12}$ cm$^3$ s$^{-1}$ \cite{Stair et al., 1985}, $3.5 \times 10^{-12}$ cm$^3$ s$^{-1}$ \cite{Sharma, 1987}, $(3 - 9) \times 10^{-12}$ cm$^3$ s$^{-1}$ \cite{Sharma and Wintersteiner, 1990}. These studies gave values of $k_{ATM}$ that are 1–2 orders of magnitude greater than values recommend earlier \cite{Crutzen, 1970; Taylor, 1974}. Later analyses of space-based observations have given values around $6 \times 10^{-12}$ (cm$^3$ s$^{-1}$) \cite{Wintersteiner et al., 1992; López-Peurtas et al., 1992; Ratkowski et al., 1994; Gusev et al., 2006; Feofilov et al., 2012 and references therein] except for the Vollmann and Grossmann \cite{1997} study giving a value of $1.5 \times 10^{-12}$ (cm$^3$ s$^{-1}$). The study of Feofilov et al. \cite{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. The study of López-Peurtas et al. \cite{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 \cite{Farmer et al., 1987; Rinsland et al., 1992} except the vmr of atomic oxygen which is taken from atmospheric models. The laboratory measurements \cite{Shved et al., 1991; Pollock et al., 1993; Khvorostovskaya et al., 2002; Castle et al., 2006, 2012] and theoretical calculations \cite{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 µm emission from the MLT region, termed $k_{ATM}$ are thus larger than the calculated and measured values by a factor of about four. Castle et al. \cite{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 $k_{LAB} = (2.5 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$ at 183 K and $(2.4 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$ at 206 K.

Unexplained rate coefficient $k_x(v_2)$ is $(5.6 \pm 1.1 - 2.5 \pm 0.4) \times 10^{-12} = (3.1 \pm 1.5) \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$ at 90 km altitude ($T \approx 183$ K) and is $(7.9 \pm 1.2 - 2.4 \pm 0.4) \times 10^{-12} = (5.5 \pm 1.6) \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$ 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 $k_{ATM}$ and 6 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$, suggested by López-Peurtas et al. [1992], and $k_{LAB} = 2.5 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$ we get $k_x = 2.0 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$, 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-Peurtas et al., 1992] or is greater [Feofilov et al., 2012] than $k_{LAB}$, contribution by major constituent atomic oxygen. As pointed out by Feofilov [2014] the GCMs use a value of $k_{GCM} = 3.0 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$ 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 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
N₂, O₂ 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 CO₂ is therefore virtually nil. However, since CO₂ is the dominant constituent in the Martian and Venusion atmospheres “hot” O atoms may play a significant role in exciting its vibrations in these planets. In the terrestrial atmosphere another reservoir of energy that either takes energy from various non-thermal 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 bending mode of CO₂ must be found to explain large $k_x$. The situation is similar to that of elevated 4.3 µm ($v_3$ mode) CO₂ emission 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 + O₃, because of its short lifetime can only transfer a very small amount of energy directly to trace specie CO₂ even though transfer of vibrational energy from higher levels ($v= 8$ and 9) of OH to $v_3$ mode of CO₂ 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 N₂ by a fast near-resonant process [Burtt and Sharma, 2008a]. The longer lived and super-thermal vibrationally excited N₂ transfers its energy, again by a fast near-resonant process [Sharma and Brau; 1967, 1969], to the $v_3$ mode of CO₂, the latter radiating around 4.3 µm. The longer lived N₂($v = 1$) molecule acts as a reservoir that takes energy from OH and stores it until it is preferentially released to CO₂.

**Hypothesis.** We advance the hypothesis that rotational degrees of freedom of N₂ and O₂ are the reservoirs that transfer their energy efficiently to the $v_2$ mode of CO₂. 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 $\mu$m emission. These rotational levels may be thermal or long lived non-thermal.

Test of the Hypothesis.

A. Thermal rotational levels. 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$_2$(01$^1$0) by N$_2$. The reaction

$$\text{CO}_2(01^10) + \text{N}_2(J) \rightarrow \text{CO}_2(00^00) + \text{N}_2(J+8) + \Delta E$$  \hspace{1cm} (2)$$

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. 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 ($\approx 0.39$ cm$^{-1}$) than N$_2$ ($\approx 1.99$ 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 of a small amount of energy from internal degrees of freedom (vibration and rotation) to translation and can therefore have much larger cross section. On the other hand, 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 183 K, temperature relevant to 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 of rate coefficient $k_4(v_2)$ 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 (2) at 168 K for all four rotational levels \( k_{VR}(N_2) \) has to be nearly equal 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 (2) the dominant mechanism for pumping 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 – 1D, using the atmospheres, provided by Feofilov and López-Puertas, give the rate coefficients \( k_{VT}(N_2) \), fifth column, and \( k_{VR}(N_2) \), last column, required by \( k_x \) given by these atmospheres. The rate coefficient \( k_{VT}(N_2) \) for the deactivation of 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 optic-acoustic effect. Taine et al. [1978, 1979], by photoacoustic method, and by Allen et al. [1980], by 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 \( 1.4 \times 10^{15} \) cm\(^3\) s\(^{-1}\) at 170 K and \( 3.7 \times 10^{15} \) cm\(^3\) s\(^{-1}\) at 295 K about one order of magnitude smaller at lower temperature and two orders magnitude smaller at higher temperature than the values given in Tables 1A – 1D. Clearly, another mechanism is needed to explain the large observed values of \( k_x = k_{ATM} - k_{LAB} \). It has already been noted that since \( k_x \) is almost equal (Tables 1C and 1D) or greater (Tables 1A and 1B) than \( k_{LAB} \) it must involve a major species with a large rate coefficient.
B. Nonthermal rotational levels. Sharma [1971] has calculated the probability per collision of the reaction

\[
\text{CO}_2(01^10) + \text{H}_2\text{O} \rightarrow \text{CO}_2(00^00) + \text{H}_2\text{O}, \quad (3)
\]
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 (\(\sigma_v\)), assuming 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\(\times 10^{-11}\) and 2.0\(\times 10^{-11}\) cm\(^3\) s\(^{-1}\) at 200 K 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\(\times 10^{-12}\) and 5.0\(\times 10^{-12}\) cm\(^3\) s\(^{-1}\) at 170 K and 295 K, respectively; probability of energy transfer per collision \(P\) at the two temperatures being 1.4\(\times 10^{-2}\) and 7.4\(\times 10^{-3}\). The inverse temperature dependence of this rate coefficient is at odds with 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,

\[
\text{CO}_2(01^10) + \text{H}_2(v = 0, J=1) \rightarrow \text{CO}_2(00^00) + \text{H}_2(v = 0, J=3) + 80.5 \text{ cm}^{-1}, \quad (4)
\]

obtaining inverse temperature dependence with \(P(300 \text{ K}) \approx 4\times 10^{-3}\) and good agreement with the then available data but smaller than the value measured by Allen et al. [1980] by a factor of about two.
The VR energy transfer processes are seen to be capable of giving rate coefficients of desired magnitude. The only molecule with large and nearly constant vmr with altitude capable of collisionally converting the vibrational energy of \( \text{CO}_2(01^10) \) into its rotational energy is \( \text{N}_2 \).

Rotationally super-thermal \( \text{N}_2 \) may be produced by collisions of fast O atoms with \( \text{N}_2 \). 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 laboratory recoil velocity of CsF obtaining excellent agreement for all eight laboratory scattering angles for which the data was available. The calculation exhibits rich rotational structure showing supernumerary and primary rainbows with rotational levels of CsF as high as \( J=194 \) populated. There is no reason why correspondingly high rotational levels of \( \text{N}_2 \) may not be populated in collisions with fast O atoms.

Duff and Sharma [1996, 1997] have calculate rate coefficient of the reaction of \( \text{N} \) with \( \text{NO} \),

\[
\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O} + 3.25 \text{ eV}, \quad (5)
\]

in the 100 – 1000 K temperature obtaining excellent agreement with the available experimental data and conforming to JPL recommendations [Sanders et al., 2011]. The calculation [Duff and Sharma, 1997] shows that product \( \text{N}_2 \) is produced in excited vibrational and rotational states; vibrational levels 2 – 7 are populated with a probability of 0.1 with rotational levels of vibrational states 1 – 4 peaked around \( J = 45 \) while those of vibrational states 5 – 8 peaked around \( J = 40 \). The VR energy transfer process

\[
\text{CO}_2(01^10) + \text{N}_2(J) \rightarrow \text{CO}_2(00^00) + \text{N}_2(J+4) + \Delta \text{E} \quad (6)
\]
is near-resonant with $|\Delta E| \leq 50 \text{ cm}^{-1}$ for seven rotational levels $36 - 42$. This process has the potential of being the sought after mechanism provided rotational levels relax in small steps ($\Delta J = -2, \Delta E \approx 230 \text{ cm}^{-1}$) with small rate coefficient. The calculation would proceed in the manner of Sharma and Kern [1971] who showed that 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

$$\text{CO}(v = 1) + \text{H}_2(v = 0, J = 2) \rightarrow \text{CO}(v = 0) + \text{H}_2(v = 0, J = 6) + 88 \text{ cm}^{-1}. \quad (7)$$

**Conclusion.** A large value of $k_\chi$ requires the rate coefficient of the unknown mechanism be equal to $k_\chi \times (\text{M vmr})/(\text{O vmr})$ where M is the species participating in the unknown mechanism. While $k_\chi$ may stay constant or increase by a factor of less than 2, the O atom vmr increases by about an order of magnitude going from 90 to 105 km altitude. Only species that stands a chance 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 ($\Delta J = -2, \Delta E \approx 230 \text{ cm}^{-1}$) with small rate coefficient.

The 15 μm (bending mode $v_2$) emission from CO$_2$ is also 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 (~ 95 % CO$_2$, a few percent 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 SCIAMACHY 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 ground-based [Sharma and Dao, 2006] and space-based [Sharma and Dao, 2005] Raman lidars proposed earlier.

**Acknowledgment.** The author is grateful to Peter Wintersteiner for many helpful discussions. The author thanks the referees for constructive comment and A. Feofilov and M. López-Puertas for supplying relevant model atmospheres.

**Table 1A –MLW Atmosphere (A. Feofilov, 19 October 2014)**

<table>
<thead>
<tr>
<th>Altitude (km)</th>
<th>Temperature (K)</th>
<th>K$_x$</th>
<th>Ovmr/N$_2$vmr</th>
<th>K$_x$(N$_2$)</th>
<th>N$_2$P4(J)</th>
<th>K$_{VR}$(N$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>91</td>
<td>169</td>
<td>3.4</td>
<td>0.023</td>
<td>0.0782</td>
<td>0.0183</td>
<td>4.27</td>
</tr>
<tr>
<td>93</td>
<td>174</td>
<td>4.1</td>
<td>0.029</td>
<td>0.1189</td>
<td>0.0206</td>
<td>5.77</td>
</tr>
<tr>
<td>96</td>
<td>185</td>
<td>4.7</td>
<td>0.043</td>
<td>0.2021</td>
<td>0.0249</td>
<td>8.12</td>
</tr>
<tr>
<td>99</td>
<td>199</td>
<td>5.0</td>
<td>0.056</td>
<td>0.280</td>
<td>0.0314</td>
<td>8.92</td>
</tr>
<tr>
<td>102</td>
<td>213</td>
<td>5.2</td>
<td>0.089</td>
<td>0.463</td>
<td>0.0381</td>
<td>12.1</td>
</tr>
<tr>
<td>105</td>
<td>227</td>
<td>5.4</td>
<td>0.129</td>
<td>0.697</td>
<td>0.0451</td>
<td>15.4</td>
</tr>
</tbody>
</table>

Rate Coefficients are in units of cm$^3$ s$^{-1}$ × 10$^{12}$.

K$_x$ = K$_{ATM}$ – K$_{Lab}$. K$_{ATM}$ provided by Dr. Feofilov (3 November 2014). K$_{Lab}$ is taken equal to 2.5 × 10$^{12}$ cm$^3$ s$^{-1}$ throughout based on the work of Castle et al. [2012].

K$_{TV}$(N$_2$) is the N$_2$ - CO$_2$($v_2$) TV 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$_x$. 


Table 1B – MLS Atmosphere (A. Feofilov, 19 October 2014)

<table>
<thead>
<tr>
<th>Altitude (km)</th>
<th>Temp (K)</th>
<th>( K_x )</th>
<th>( \text{Ovmr/N}_2\text{vmr} )</th>
<th>( K_{TV}(\text{N}_2) )</th>
<th>( [\text{N}_2\text{P}4(J)] )</th>
<th>( K_{VR}(\text{N}_2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>183</td>
<td>3.1</td>
<td>0.018</td>
<td>0.0558</td>
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</tr>
<tr>
<td>93</td>
<td>179</td>
<td>4.1</td>
<td>0.028</td>
<td>0.1148</td>
<td>0.0223</td>
<td>5.15</td>
</tr>
<tr>
<td>96</td>
<td>178</td>
<td>4.7</td>
<td>0.05</td>
<td>0.235</td>
<td>0.0218</td>
<td>10.8</td>
</tr>
<tr>
<td>99</td>
<td>182</td>
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<td>0.079</td>
<td>0.4029</td>
<td>0.0237</td>
<td>17.0</td>
</tr>
<tr>
<td>102</td>
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<td>0.156</td>
<td>0.8112</td>
<td>0.0277</td>
<td>29.3</td>
</tr>
<tr>
<td>105</td>
<td>206</td>
<td>5.4</td>
<td>0.219</td>
<td>1.1826</td>
<td>0.0372</td>
<td>31.8</td>
</tr>
</tbody>
</table>

\( K_x = K_{\text{ATM}} - K_{\text{Lab}} \). \( K_{\text{ATM}} \) provided by Dr. Feofilov (3 November 2014). \( K_{\text{Lab}} \) is taken equal to \( 2.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \) throughout based on Castle et al. [2012].

\( K_{TV}(\text{N}_2) \) is the \( \text{N}_2 - \text{CO}_2(\nu_2) \) TV rate coefficient needed to explain \( K_x \).

\( \text{N}_2\text{P}4(J) \) is the fraction of \( \text{N}_2 \) molecules in the four rotational levels 15 – 18.

\( K_{VR}(\text{N}_2) \) is the \( \text{N}_2 - \text{CO}_2(\nu_2) \) VR rate coefficient needed to explain \( K_x \).

Table 1C – Polar Summer SABER Model Atmosphere (López-Puertas, 11 Nov 2014)

<table>
<thead>
<tr>
<th>Altitude (km)</th>
<th>Temperature (K)</th>
<th>( K_x )</th>
<th>( \text{Ovmr/N}_2\text{vmr} )</th>
<th>( K_{TV}(\text{N}_2) )</th>
<th>( \text{N}_2\text{P}4(J) )</th>
<th>( K_{VR}(\text{N}_2) )</th>
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<tr>
<td>95</td>
<td>179.7</td>
<td>2.0</td>
<td>0.0198</td>
<td>0.0396</td>
<td>0.02264</td>
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<tr>
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<td>0.163</td>
<td>0.326</td>
<td>0.08339</td>
<td>3.91</td>
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</tbody>
</table>

\( K_{\text{ATM}} = 4.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \) is average of \( (3 – 6) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \) given by López-Puertas et al. [1992].

Table 1D – Polar Winter SABER Model Atmosphere (López-Puertas, 11 Nov 2014)

<table>
<thead>
<tr>
<th>Altitude (km)</th>
<th>Temperature (K)</th>
<th>( K_x )</th>
<th>( \text{Ovmr/N}_2\text{vmr} )</th>
<th>( K_{TV}(\text{N}_2) )</th>
<th>( \text{N}_2\text{P}4(J) )</th>
<th>( K_{VR}(\text{N}_2) )</th>
</tr>
</thead>
<tbody>
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<td>0.025</td>
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<td>0.05162</td>
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<td>0.108</td>
<td>0.1192</td>
<td>0.906</td>
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References


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