On the possibly missing mechanism of 15 μm emission in the mesosphere-lower thermosphere (MLT)

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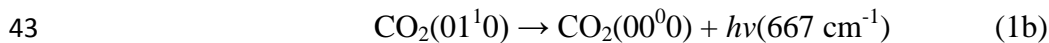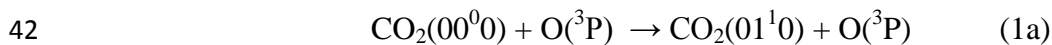
Abstract. Accurate knowledge of the rate as well as the mechanism of excitation of the bending mode of CO_2 is necessary for reliable modeling of the mesosphere- lower thermosphere (MLT) region of the atmosphere. Assuming the excitation mechanism to be thermal collisions with atomic oxygen the rate coefficient derived from the observed 15 μm emission by space-based experiments ($k_{ATM} = 6.0 \times 10^{-12}$ $cm^3 s^{-1}$) differ 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 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 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 super-thermal population and are long lived. Since atomic oxygen plays a critical role in

25   the mechanisms discussed here, it suggested that its density be determined experimentally by

26   ground and space based Raman lidars proposed earlier.

27   **Key words**: 15 μm emission, CO_2, N_2, O, rotation, vibration, near-resonant energy transfer.

28   **Introduction.** The 15 μm emission from CO_2 is the dominant cooling mechanism in the MLT

29   region [*Gordiets et al.*, 1982; *Dickinson*, 1984; *Sharma and Wintersteiner*, 1990; *Wintersteiner et*

30   *al., 1992; López-Peurtas et al., 1992; Sharma and Roble*, 2002]. The magnitude of this cooling

31   impacts both the temperature and height of the terrestrial mesopause [*Bougher et al*., 1994]. This

32   process is also important in the Martian and Venusian atmospheres [*Bougher et al., 1999*],

33   especially the latter where it acts as a thermostat during the long day (243 times the length of

34   terrestrial day). The 15 μm emission from CO_2 has been used by a number of satellites

35   [*Offermann et al*., 1999; *Russell et al*., 1999; *Fischer et al.*, 2008] to retrieve atmospheric

36   temperature as a function of altitude. Finding the mechanism leading to this emission is

37   therefore very important.

38   Translational energy (heat) is collisionally converted into vibrational energy of the bending mode

39   of CO_2. A fraction of the resulting vibrational energy is radiated away to space cooling the

40   atmosphere. The dominant mechanism for this conversion is believed to be the collisions

41   between CO_2 and O,

$$CO_2(00^00) + O(^3P) \rightarrow CO_2(01^10) + O(^3P) \qquad (1a)$$

42

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

43

44   This process is endothermic by the energy of the emitted photon, 667 cm^{-1} (~15 μm). In

45   chemical literature, the rate coefficients of the reactions are given in the exothermic direction

46   (reverse of equation 1a) and we will follow that convention. The room temperature value of the

47   rate coefficient k_{ATM} for the exothermic process derived by modeling the 15 μm emission,

48   observed by Spectral Infrared Rocket Experiment (SPIRE) [*Stair et al.*, 1985], from the MLT

49   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*

50   *et al.,* 1985], 3.5×10^{-12} cm^3 s^{-1} [*Sharma,* 1987], $(3-9)\times10^{-12}$ cm^3 s^{-1} [*Sharma and Wintersteiner*,

51   1990]. These studies gave values of k_{ATM} that are $1-2$ orders of magnitude greater than values

52   recommend earlier [*Crutzen*, 1970; *Taylor*, 1974]. Later analyses of space-based observations

53   have given values around 6×10^{-12} (cm^3 s^{-1}) [*Wintersteiner et al., 1992*; *López-Peurtas et al.,*

54   *1992; Ratkowski et al.*, 1994; *Gusev et al.*, 2006; *Feofilov et al.*, 2012 and references therein]

55   except for the *Vollmann and Grossmann* [1997] study giving a value of 1.5×10^{-12} (cm^3 s^{-1}). The

56   study of *Feofilov et al.* [2012] determined the rate coefficient by coincidental SABER/TIMED

57   and Fort Collins sodium lidar observations in the MLT region and arrived at values of

58   $(5.5\pm1.1)\times10^{-12}$ cm^3 s^{-1} at 90 km altitude and $(7.9\pm1.2)\times10^{-12}$ cm^3 s^{-1} at 105 km with an average

59   value of $(k_{ATM} = 6.5\pm1.5)\times10^{-12}$ cm^3/s. The study of *López-Peurtas et al.* [1992] "suggests a

60   value of between 3 and 6×10^{-12} cm^3 s^{-1} at 300 K" and temperature "independent or negative

61   temperature dependence". This study derives the values for all input parameters from

62   ATMOS/Spacelab 3 observations [*Farmer et al.,* 1987; *Rinsland et al.*, 1992] except the vmr of

63   atomic oxygen which is taken from atmospheric models.

64   The laboratory measurements [*Shved et al.*, 1991; *Pollock et al.*, 1993; *Khvorostovskaya et al.*,

65   2002; *Castle et al.*, 2006, 2012] and theoretical calculations [*de Lara-Castells et al.*, 2006, 2007]

66   give room temperature values of $k_{LAB} \approx (1.5-2.5)\times10^{-12}$ (cm^3 s^{-1}). The values of k_{VT} determined

67   by modeling 15 μm emission from the MLT region, termed k_{ATM}. are thus larger than the

68   calculated and measured values by a factor of about four. *Castle et al.* [2012] have measured the

69   deactivation of $CO_2(v_2)$ by $O(^3P)$ in the 142 - 490 K temperature range obtaining values of the

70   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.

71   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

72   km altitude (T ≈ 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

73   altitude [Table 1B]. $k_x(v_2)$ increases by a factor of 1.8 in going from 90 km altitude to 105 km

74   altitude (≈206 K) showing a steep variation with altitude. Using the average of the value of k_{ATM}

75   3 and 6×10^{-12} cm^3 s^{-1}, 4.5×10^{-12} cm^3 s^{-1}, suggested by *López-Peurtas et al.* [1992], and $k_{LAB} =$

76   2.5×10^{-12} cm^3 s^{-1} we get $k_x = 2.0 \times 10^{-12}$ cm^3 s^{-1}, a smaller value independent of temperature

77   (altitude). It should be noted that the contribution to the rate coefficient k_{ATM} by unknown

78   mechanism k_x nearly equals [*López-Peurtas et al.*, 1992] or is greater [*Feofilov et al.,* 2012] than

79   k_{LAB}, contribution by major constituent atomic oxygen. As pointed out by *Feofilov* [2014] the

80   GCMs use of a value of $k_{GCM} = 3.0 \times 10^{-12}$ cm^3 s^{-1} for this rate coefficient [*Bougher et al., 1999*]

81   further complicates the problem. To resolve this difficult problem we break it into pieces and

82   attempt to find the cause of discrepancy between k_{ATM} and k_{LAB}.

83   To resolve the discrepancy between k_{ATM} and k_{LAB} *Feofilov et al.* [2012] postulate that

84   nonthermal, or "hot", oxygen atoms, produced in the MLT region by photolysis of O_2 and

85   dissociative recombination of O_2^+, etc., may serve as an additional source of $CO_2(v_2)$ level

86   excitation. These authors have derived CO_2 volume mixing ratio (vmr) parts per million by

87   volume (ppmv) in the MLT region for the time of their experiment from atmospheric models as

88   well as space based observations. The average vmr, according to MLW atmosphere is about 268

89   ppmv at 90 km altitude and about 105 ppmv at 105 km altitude in general agreement with the

90   values given by *Rinsland et al*. [1992]. This means that for every collision a "hot" oxygen atom

91   undergoes with CO_2, it must undergo ($10^6/268=$) 3731 collisions at 90 km altitude and

92   ($10^6/105=$) 9524 collisions at 105 km altitude with other atmospheric constituents, mostly with

93   N$_2$, O$_2$ and O. Solution of the time dependent Boltzmann equation with realistic potential

94   functions [*Dothe et al.,* 1997] has shown that a 1 eV "hot" atom loses most of its energy in a few

95   collisions. The chance of a "hot" atom colliding with CO$_2$ is therefore virtually nil. However,

96   since CO$_2$ is the dominant constituent in the Martian and Venusion atmospheres "hot" O atoms

97   may play a significant role in exciting its vibrations in these planets. In the terrestrial

98   atmosphere another reservoir of energy that either takes energy from various non-thermal energy

99   sources, e.g., 'hot" O atoms, and that may or may not be in local thermodynamic equilibrium but

100   one that readily transfers energy preferentially to bending mode of CO$_2$ must be found to explain

101   large k_x. The situation is similar to that of elevated 4.3 μm (v_3 mode) CO$_2$ emission from the

102   hydroxyl layer in the nocturnal mesosphere [*Kumer et al.*, 1978; *López-Puertas et al.*, 2004].

103   Highly vibrationally excited OH, produced by the reaction of H + O$_3$, because of its short

104   lifetime can only transfer a very small amount of energy directly to trace specie CO$_2$ even though

105   transfer of vibrational energy from higher levels (v= 8 and 9) of OH to v_3 mode of CO$_2$ is a fast

106   near-resonant process [*Burtt and Sharma*, 2008b]. The vibrational energy from higher levels

107   (v= 8 and 9) of OH is instead transferred to N$_2$ by a fast near-resonant process [*Burtt and*

108   *Sharma*, 2008a]. The longer lived and super-thermal vibrationally excited N$_2$ transfers its

109   energy, again by a fast near-resonant process [*Sharma and Brau*; 1967, 1969], to the v_3 mode of

110   CO$_2$, the latter radiating around 4.3 μm. The longer lived N$_2$($v = 1$) molecule acts as a reservoir

111   that takes energy from OH and stores it until it is preferentially released to CO$_2$.

112   **Hypothesis.** *We advance the hypothesis that rotational degrees of freedom of N$_2$ and O$_2$ are the*

113   *reservoirs that transfer their energy efficiently to the v_2 mode of CO$_2$. High rotational levels of*

114   *these reservoirs by a near-resonant rotation-to-vibration energy transfer process are responsible*

115 *for efficiently exciting the bending (v₂) mode of CO₂ leading to 15 μm emission. These rotational*

116 *levels may be thermal or long lived non-thermal.*

117 **Test of the Hypothesis.**

118 **A. Thermal rotational levels.** Since the N_2 density at the altitudes under consideration is

119 much greater than O_2 density we provide justification for the deactivation of $CO_2(01^10)$

120 by N_2. The reaction

121 $$CO_2(01^10) + N_2(J) \rightarrow CO_2(00^00) + N_2(J+8) + \Delta E \qquad (2)$$
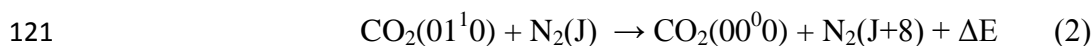
122 is exothermic by 46 cm^{-1} and 14 cm^{-1} for J = 15 and 16 and endothermic by 17 cm^{-1} and 49 cm^{-1}

123 for J = 17 and 18. The CO_2 molecule, in the dipole-hexadecapole moment and quadrupole-

124 hexadecapole moment interactions involved undergoes $\Delta J = \pm3, \pm2, \pm1, 0$ in the process. Since

125 CO_2 has a much smaller rotational constant (≈ 0.39 cm^{-1}) than N_2 (≈ 1.99 cm^{-1}) we, for the rough

126 estimate, ignore the contributions of its rotational transitions to the energy transfer process.

127 The near-resonant processes, mediated by long-range multipole and dispersion interactions,

128 transfer of a small amount of energy from internal degrees of freedom (vibration and rotation) to

129 translation and can therefore have much larger cross section. On the other hand, processes that

130 require transfer of large amount of energy from internal (vibration and rotation) degrees of

131 freedom to translation and can be mediated only by short range repulsive forces tend to have

132 smaller cross section. This is the rationale for selecting $\Delta J = 8$ transitions since they are both

133 near-resonant and can be mediated by long-range forces. At 183 K, temperature relevant to MLS

134 atmosphere (Table 1B), at about 90 km altitude, about 2.4% of the N_2 molecules reside in one of

135 these four rotational levels. The density of N_2 in these four thermalized rotational levels is

136 (0.0241/0.018 =) 1.34 times that of atomic oxygen. The unexplained of rate coefficient $k_x(v_2)$ at

6

137 90 km altitude for pumping of the v_2 mode of CO_2 is $(3.1\pm1.5)\times10^{-12}$ $cm^3 s^{-1}$. The sum of the rate

138 coefficients of reaction (2) at 168 K for all four rotational levels $k_{VR}(N2)$ has to be nearly equal

139 or greater than $(3.1\pm1.5)\times10^{-12}/1.34 = (2.32\pm1.1)\times10^{-12}$ $cm^3 s^{-1}$ to make reaction (2) the dominant

140 mechanism for pumping the v_2 mode of CO_2. Since only 2.4 % of the N_2 molecules participate

141 in the RV energy transfer process the rate coefficient for deactivation of $CO_2(v_2)$ by N_2 would be

142 $k_{VT}(N2) = ((2.32 \pm 1.1)\times0.024)\times10^{-12} = (5.6 \pm 2.6)\times10^{-14}$. A larger calculated rate coefficient

143 k_{N2} would not be a problem since the v_2 mode of CO_2 at least up to 90 km altitude is in local

144 thermodynamic equilibrium (LTE), i.e., its vibrational temperature is nearly the same as the

145 translational temperature [*Feofilov et al.*, 2012; *López-Puertas et al.*, 1992; *Stair et al.*, 1985].

146 Tables 1A – 1D, using the atmospheres, provided by Feofilov and López-Puertas, give the rate

147 coefficients $k_{VT}(N2)$, fifth column, and $k_{VR}(N2)$, last column, required by k_x given by these

148 atmospheres. The rate coefficient $k_{VT}(N2)$ for the deactivation of bending mode of CO_2 by N_2 at

149 low temperatures has been measured at room temperature by Merrill and Amme [1969] using

150 ultrasonic velocity dispersion measurements and by Cannemeyer and De Vries [1974] using

151 optic-acoustic effect. *Taine et al.* [1978, 1979], by photoacoustic method, and by *Allen et al.*

152 [1980], by laser fluorescence technique, have measured $k_{VT}(N2)$ at low temperatures. These

153 studies are in general agreement with that of *Allen et al.* [1980] giving $k_{VT}(N2)$ equal to 1.4×10^{-15}

154 $cm^3 s^{-1}$ at 170 K and 3.7×10^{-15} $cm^3 s^{-1}$ 295 K about one order of magnitude smaller at lower

155 temperature and two orders magnitude smaller at higher temperature than the values given in

156 Tables 1A – 1D. Clearly, another mechanism is needed to explain the large observed values of

157 $k_x \equiv k_{ATM} - k_{LAB}$. It has already been noted that since k_x is almost equal (Tables 1C and 1D) or

158 greater (Tables 1A and 1B) than k_{LAB} it must involve a major species with a large rate

159 coefficient.

160   **B. Nonthermal rotational levels.** *Sharma* [1971] has calculated the probability per

161   collision of the reaction

162    $$CO_2(01^10) + H_2O \rightarrow CO_2(00^00) + H_2O, \quad (3)$$
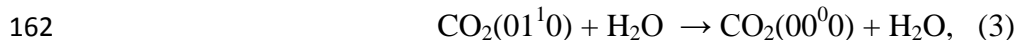
163   a much studied process because of its importance in CO_2 lasers, assuming a vibration-to-rotation

164   (VR) energy transfer (ET) mechanism mediated by long range multipolar interactions. In spite of

165   a large scatter in the experimental data, a situation typical of low temperature experiments

166   involving water vapor, the agreement is quite good. The calculated probability per collision is

167   0.06 at 200 K and 0.08 at 300 K. The rate coefficients (σv), assuming gas kinetic rate of 2×10^{-10}

168    $cm^3 \, s^{-1}$ 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 K and

169   300 K, respectively.

170   *Allen et al.* [1980] have measured rate coefficients for the deactivation of the bend-stretch mode

171   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}

172    $cm^3 \, s^{-1}$ at 170 K and 295 K, respectively; probability of energy transfer per collision P at the two

173   temperatures being 1.4×10^{-2} and 7.4×10^{-3}. The inverse temperature dependence of this rate

174   coefficient is at odds with Landau-Teller TV energy transfer mechanism and very much in

175   accord with the near-resonant energy transfer mechanism [*Sharma and Brau*; 1967, 1969].

176   *Sharma* [1969] has calculated the deactivation of $CO_2(v_2)$ by H_2 assuming a near-resonant VR

177   energy transfer mechanism mediated by dipole-quadrupole interaction,

178    $$CO_2(01^10) + H_2(v = 0, J=1) \rightarrow CO_2(00^00) + H_2(v = 0, J=3) + 80.5 \, cm^{-1}, \quad (4)$$
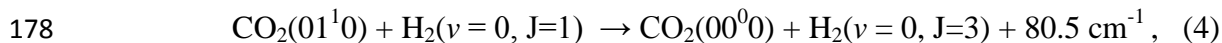
179   obtaining inverse temperature dependence with $P(300 \text{ K}) \approx 4 \times 10^{-3}$ and good agreement with the

180   then available data but smaller than the value measured by *Allen et al.* [1980] by a factor of

181   about two.

182   The VR energy transfer processes are seen to be capable of giving rate coefficients of desired

183   magnitude. The only molecule with large and nearly constant vmr with altitude capable of

184   collisionally converting the vibrational energy of $CO_2(01^10)$ into its rotational energy is N_2.

185   Rotationally super-thermal N_2 may be produced by collisions of fast O atoms with N_2. *Sharma*

186   *and Sindoni* [1993] have calculated the differential cross-section of Ar-CsF colliding with 1.0

187   initial relative translational energy as a function of laboratory recoil velocity of CsF obtaining

188   excellent agreement for all eight laboratory scattering angles for which the data was available.

189   The calculation exhibits rich rotational structure showing supernumerary and primary rainbows

190   with rotational levels of CsF as high as J=194 populated. There is no reason why

191   correspondingly high rotational levels of N_2 may not be populated in collisions with fast O

192   atoms.

193   *Duff and Sharma* [1996, 1997] have calculate rate coefficient of the reaction of N with NO,

194   $$N + NO \rightarrow N_2 + O + 3.25 \text{ eV},   (5)$$

195   in the 100 – 1000 K temperature obtaining excellent agreement with the available experimental

196   data and conforming to JPL recommendations [*Sanders et al.*, 2011]. The calculation [*Duff and*

197   *Sharma*, 1997] shows that product N_2 is produced in excited vibrational and rotational states;

198   vibrational levels 2 – 7 are populated with a probability of 0.1 with rotational levels of

199   vibrational states 1 – 4 peaked around J = 45 while those of vibrational states 5 – 8 peaked

200   around J = 40. The VR energy transfer process

201   $$CO_2(01^10) + N_2(J) \rightarrow CO_2(00^00) + N_2(J+4) + \Delta E   (6)$$
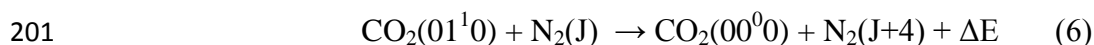
202   is near-resonant with $|\Delta E| \leq 50$ cm^{-1} for seven rotational levels $36 - 42$. This process has the

203   potential of being the sought after mechanism provided rotational levels relax in small steps (ΔJ

204    $= -2, \Delta E \approx 230$ cm^{-1}) with small rate coefficient. The calculation would proceed in the manner of

205   *Sharma and Kern* [1971] who showed that greater rate of deactivation of vibrationally excited

206   CO by para-hydrogen over ortho-hydrogen is due to the near-resonant VR process mediated by

207   multipolar interactions

208    $$CO(v = 1) + H_2(v = 0, J = 2) \rightarrow CO(v = 0) + H_2(v = 0, J = 6) + 88 \text{ cm}^{-1}. \quad (7)$$
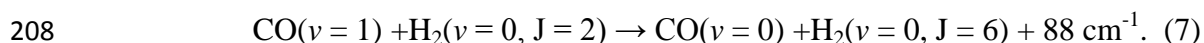
209   **Conclusion.** A large value of k_x requires the rate coefficient of the unknown mechanism be

210   equal to $k_x \times$ (M vmr)/(O vmr) where M is the species participating in the unknown mechanism.

211   While k_x may stay constant or increase by a factor of less than 2, the O atom vmr increases by

212   about an order of magnitude going from 90 to 105 km altitude. Only species that stands a chance

213   meeting these stringent requirements is N_2, its vmr while not increasing stays nearly constant at

214   about 0.78. It is shown that the $CO_2(v_2) - N_2$ near-resonant VR rate coefficients could be large

215   enough to meet the requirements. In the thermal atmosphere the VR processes lead to VT rate

216   coefficients that are $1 - 2$ orders of magnitude too large. Rotationally super-thermal N_2,

217   produced by collisions of fast O atoms with N_2 or by the N + NO reaction or any other

218   mechanism hold out hope if these rotational levels relax in small steps ($\Delta J = -2, \Delta E \approx 230$ cm^{-1})

219   with small rate coefficient.

220   The 15 μm (bending mode v_2) emission from CO_2 is also important cooling mechanism in the

221   atmospheres of Venus and Mars [*Bougher et al., 1999*], especially the former where it acts as a

222   thermostat during the long day (243 times the length of the terrestrial day). The atmospheres of

223   Venus and Mars are similar (~ 95 % CO_2, a few percent N_2) and in these atmospheres direct

224   excitation of CO_2 vibrations by fast O atoms may be an important cooling mechanism.

225   The density of atomic oxygen plays very important role in cooling planetary atmospheres.

226   Recently published values of atomic oxygen density [*Kaufmann et al.*, 2014] derived from

227   nighttime limb measurements of atomic oxygen green line intensity in the mesopause region, by

228   SCIAMACHY instrument on the European Environmental Satellite, are "at least 30% lower than

229   atomic oxygen abundances obtained from SABER" instrument on the TIMED satellite. Perhaps

230   it is time that atomic oxygen density is measured using ground-based [*Sharma and Dao*, 2006]

231   and space-based [*Sharma and Dao*, 2005] Raman lidars proposed earlier.

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

Altitude (km)	Temperature (K)	K_x	Ovmr/N_2vmr	$K_x(N_2)$	N_2P4(J)	$K_{VR}(N_2)$
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

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

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

239   $K_{TV}(N_2)$ is the N_2 - $CO_2(v_2)$ TV rate coefficient needed to explain K_x.

240   N_2P4(J) is the fraction of N_2 molecules in the four rotational levels 15 – 18.

241   $K_{VR}(N_2)$ is the N_2 - $CO_2(v_2)$ VR rate coefficient needed to explain K_x.

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

Altitude (km)	Temp (K)	K_x	Ovmr/N_2vmr	K_{TV}(N2)	[N2P4(J)]	K_{VR}(N_2)
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

244 $K_x = K_{ATM} − K_{Lab}$. K_{ATM} provided by Dr. Feofilov (3 November 2014). K_{Lab} is taken equal to 2.5×10^{12} cm^3 s^{-1}
245 throughout based on Castle et al. [2012].

246 K_{TV}(N_2) is the N_2 - CO_2(v_2) TV rate coefficient needed to explain K_x.

247 N_2P4(J) is the fraction of N_2 molecules in the four rotational levels 15 – 18.

248 K_{VR}(N_2) is the N_2 - CO_2(v_2) VR rate coefficient needed to explain K_x.

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

Altitude (km)	Temperature (K)	K_x	Ovmr/N_2vmr	K_{TV}(N_2)	N2P4(J)	K_{VR}(N_2)
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

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

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

Altitude (km)	Temperature (K)	K_x	Ovmr/N_2vmr	K_{TV}(N_2)	N2P4(J)	K_{VR}(N_2)
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

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