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Interactive Comment

Interactive comment on "Technical Note: A new mechanism of 15 μm emission in the mesosphere-lower thermosphere (MLT)" *by* R. D. Sharma

Anonymous Referee #3

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Review of the manuscript "A new mechanism of 15 μm emission in the mesosphere-lower thermosphere (MLT)" by R. D. Sharma, submitted for publication in the Atmospheric Chemistry and Physics as a technical note.

The paper addresses the mechanisms of excitation of the CO2(v2) bending mode, which are crucially important both for modeling the energy budget of the mesosphere-lower thermosphere (MLT) and for interpretation of the satellite observation of these region. The author suggests an excitation mechanism, which supposedly may explain a significant difference between the laboratory measured rate coefficient for the CO2(v2) quenching by collisions with thermal oxygen atoms and the one derived from the 15 μm

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Interactive Discussion

Discussion Paper

emissions measured in space born experiments. It is assumed that thermal collisions with N2, mediated by a near-resonant vibration to rotation energy transfer process, efficiently quench CO2(v2) by transferring energy to high rotational levels of thermal N2.

I recommend the paper for publication in ACP if my major concerns outlined below are properly addressed.

General comments

I avoid discussing here the concern that processes proposed to explain the gap between the results of laboratory measurements and atmospheric estimates of the rate coefficient under consideration do not explain the difference between the value typically used in the GCMs and the one retrieved from atmospheric observations. This problem is discussed in detail in the review by A. Feofilov and I completely agree with this discussion and its conclusion.

1. My major point of concern is as follows. The collisional quenching of CO2(v2) by thermal N2 is accounted for in any work on the non-LTE modeling of the CO2 15 μm emissions mentioned by the author including those used for fitting the 15 μm emissions space observations to derive the CO2(v2) – O3P quenching rate coefficient. The process is treated as a pure vibration-transnational (VT) one, see for instance [1], with the rate coefficients taken from measurements made in 1970s-80s [2-4] for temperatures down to 160-170 K.

In photo-acoustic studies [2,3] the 15 μm radiation modulated at a certain frequency was absorbed by CO2, highly diluted in a diatomic gas which lead to population mainly of the CO2 (010) level.

Energy transfers induced by collisions occurred between rotational-vibrational (RV) and rotational-translational (RT) degrees of freedom; it resulted in a periodic variation of pressure in the cell at the same frequency. The phase shift between the absorbed

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radiative power and the periodic excess pressure in the cell was measured. The collisional rate was determined from the phase shift changes with pressure at a given frequency.

The physics of these experiments and the kinetic models used in the analysis imply that the retrieved value for CO2/N2 mixtures is a total rate coefficient for the sum of all (RV)-(RT) energy exchange processes of type:

CO2(010,j) + N2(0,J) $\rightarrow$ CO2(000,j') + N2(0,J')

(for various possible combinations of j, j', J and J') involved in the quenching the vibrational 010 state of CO2, including those near-resonant ones which are discussed in the paper. This sum was obviously interpreted as a total VT rate for CO2(010) quenching by N2. The same conclusion is also true for the fluorescence measurements [4] which delivered rate coefficients close to those of [2, 3]. It should be noted, that if the processes considered in the manuscript dominated the CO2(010)-N2 quenching studied in [2-4], then the rate coefficients obtained in these studies should be close to the coefficients suggested by the manuscript author for these near-resonant reactions.

From this point of view, the manuscript is missing an explanation why new processes of energy transfer suggested by the author need to be added in calculations although they seem to be part of exchanges already taken into account in the current models of the 15 μm emission.

2. I also do not understand why does the author consider in detail the rotational structure of the N2 ground level and at the same time he completely ignores rotational distribution of the CO2(v2) molecules. To my mind, accounting for rotational excitation of CO2 should change the resonance conditions described in the paper. Can the author clarify this point?

Minor comments

none

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