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PFS/MEX limb observations of 4.3-µm CO_2 non-LTE emission in the atmosphere of Mars

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ABSTRACT

We present PFS-MEX limb observations of the CO_2 non-local thermodynamic equilibrium (non-LTE) emission at 4.3 µm in the atmosphere of Mars collected in more than six Martian years. With unprecedented spatial and temporal coverage, and relatively high spectral resolution, this unique dataset promises to improve our understanding of the upper atmosphere of Mars. The former allows analyses of the emission as a function of tangent altitude, solar zenith angle, season, latitude, local time, and thermal condition of the atmosphere. The latter allows unambiguous identification of several emission bands of different isotopologues. We selected observations in the altitude range 50–200 km.

No emission was detected for altitudes higher than 170 km. The spectral shape of the non-LTE emission changes dramatically with the altitude of the tangent point, reflecting the different contribution of the major and minor CO_2 bands and isotopologues to the total emission at different heights. For altitudes higher than 130 km the observed spectrum is dominated by the second hot (SH) bands of the main isotopologue $^{12}C^{16}O_2$ (also referred to as 626 SH). At lower altitudes, the contribution of the isotopic $^{13}C^{16}O_2$ second hot bands (636 SH) to the observed spectrum gradually increases, and is maximum around 70–80 km. Similar consideration apply to the fourth hot bands of the $^{12}C^{16}O_2$ (626 FRH), and particularly those from the (2001x) levels, whose contribution is maximum around 80–90 km. The 626 SH bands can be observed up to an altitude 160–170 km, and their emission is peaked around 120–130 km. The 626 FRH and 636 SH bands are not observed above 130–140 km. Both the first hot (FH) and the fundamental band (FB) of the main isotopologue show a peculiar behavior. Indeed, these emissions can be observed at all altitudes, from 50 km up to 170 km. The intensity of the FH band increases linearly with decreasing height, while the intensity of the FB band is essentially constant at all altitudes, and rapidly decreases above 150 km.

For a fixed altitude, the solar zenith angle (SZA) is the main parameter affecting the intensity and the spectral shape of the non-LTE emission. For SZA between 0 and 40° the intensity of the emission does not show significant variations. For SZAs larger than 40° the observed emission decreases rapidly with increasing SZA, following a cosine-like relation. The different illumination also affects the spectral shape of the non-LTE emission spectrum. High incidence angles tend to increase the relative contribution of weaker bands compared to stronger/optically thicker bands. For a fixed SZA, we found variation of the intensity of the emission with local time, in response to variations of the thermal structure of the atmosphere.

Latitudinal variation of the intensity of the CO_2 non-LTE are also investigated. The maximum intensity is observed around the sub-solar latitudes, where the solar flux is maximum. The intensity of the emission and the altitude at which the maximum emission is observed also changes with the season. The altitude where the maximum intensity of the 626 SH bands is observed decreases from 120–130 km at the perihelion (Ls = 251°), down to ~85 km at the southern winter solstice (Ls = 90°). This is explained by the variability of the thermal structure (scale heights) of the Martian atmosphere with the season, as a response to the changing solar flux. The altitude of a given pressure level depends on the thermal structure of the atmosphere which, in turn, depends on the season. On the contrary, the pressure level of the peak emission does not depend on the scale heights, as it is mainly controlled by the CO_2 column density above the peak.

These results, while on one hand confirm and provide more insights and constraints to some aspects of the non-LTE processes on Mars, on the other hand further stimulate and challenge current theoretical models,

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possibly bringing closer the moment in which the measurements could be inverted to derive important information about the upper mesosphere and lower thermosphere of Mars.

1. Introduction

Non Local Thermodynamic Equilibrium (non-LTE) processes play a key role in the cooling and heating rate of the mesosphere and lower thermosphere of Mars. The knowledge of this mechanism is extremely important for the study of the upper atmospheric layers, and it may also affect the lower part of the atmosphere. Indeed, the meteorological processes on Mars, unlike the Earth, appear to have a considerably larger vertical extension, probably involving the top of the neutral atmosphere up to 120 km (Bertaux et al. 2006).

At these altitudes the radiative budget of the atmosphere is determined by the direct absorption of sunlight in the near-IR region between 1 and 5 µm and the cooling via non-LTE emission of the 15-µm CO_2 bands (López-Puertas and López-Valverde, 1995). Particularly important is the absorption of the solar radiation in the range 1.2 - 2.7 µm because a major part of this energy is reemitted in cascade at 4.3 µm and 10 µm (Lopez-Puertas and Taylor, 2001). Vibrational- vibrational (V-V) collisions – where vibrational quanta are exchanged between the colliding molecules – redistribute the absorbed solar energy in a variety of vibrational states (Lopez-Puertas and Taylor, 2001). Collisions occur preferentially between excited and ground state CO_2 molecules rather than between two molecules in an excited state because the population of the carbon dioxide ground state is larger. V-V collisions involve both the major and minor CO_2 isotopes (Lopez-Puertas and Taylor 2001), therefore the contribution of higher order, weak isotopic transitions becomes important. These processes need to be understood in details in order to perform meaningful simulations of the radiative balance of the middle and upper atmosphere of Mars and to extend the present parameterizations of the infrared radiative cooling/heating currently in use in Martian Global Circulation Models (GCMs).

An accurate analysis of the non-LTE emissions requires the combined solution of the problem of ro-vibrational relaxation for a large number of excited vibrational states of CO_2 and CO isotopic molecules, and the radiative transfer equation for a very large number of ro-vibrational lines. To test the available theoretical tools, a complete dataset of observations of the upper Martian atmosphere is extremely important. However, only a few studies of the non-LTE behavior of CO_2 in the mesosphere and thermosphere of Mars exist so far. CO_2 fluorescence emission at 4.3 µm has been observed with the Infrared Space Observatory (ISO) (Lellouch et al., 2000) and it had been suggested to be originated by excited vibrational transitions involving the CO_2 second hot (SH) band. A more detailed study of the CO_2 non-LTE emission at 10 µm has been performed by Maguire et al. (2002) with the Thermal Emission Spectrometer (TES) onboard Mars Global Surveyor (MGS). Limb spectral measurements of the upper atmosphere provided a global map of the 10 µm non-LTE emission up to an altitude of 120 km for the different seasonal periods. Theoretical calculations of the CO_2 atmospheric emissions at 10 µm in the upper atmospheres of Mars and Venus have been performed by Lopez-Valverde et al. (2011a).

Observations of non-LTE radiation at 4.3 µm were carried out with the Planetary Fourier Spectrometer (PFS, Formisano et al. 2005a) and the Observatoire pour la Minéralogie, l’ Eau, les Glaces et l’ Activité (OMEGA, Bibring et al., 2004) onboard the Mars Express (MEx) mission. Early PFS nadir and limb measurements were used for a first validation test of the non-LTE model (Formisano et al., 2005b; Lopez-Valverde et al., 2005, Gilli et al., 2011), confirming that the main contribution to the spectrum was originated by the emission of the second hot bands of the main CO_2 isotope. PFS limb observations of two case orbits have been discussed by Formisano et al. (2006). The authors detected several emitting bands in the PFS spectra, including the second hot band for the 626 and 636 molecule, and other unidentified minor bands or lines observed for the first time on Mars. PFS observations also indicated that both the intensity and the height of peak emission varies with latitude (Formisano et al., 2006). Similar results have been recently reported by OMEGA observations (Piccialli et al., 2016) and strong non-LTE CO and CO_2 daytime limb emissions were also observed on Venus by the Visible and Infrared Thermal Imaging Spectrometer (VIRTIS) on board the European Venus Express mission (Gilli et al., 2009, 2015).

The advantage of limb measurements is twofold. First, they allow to locate the height above the surface where the non-LTE emission occurs. Second, it is possible to detect the emission from weaker transitions compared to the nadir data, which are useful to put more stringent constraints on the model. Indeed, Formisano et al. (2006) reported the detection of isotopic bands in addition to the CO_2 SH bands, and a variability of the emission spectra as a function of the altitude of the tangent point. The SH bands dominate the spectra at high altitudes. However, to date, several features observed in the spectra still remain unidentified, especially in the 2280–2310 cm^{-1} spectral region. The identification of all the weak and isotopic bands still requires more observations and detailed theoretical work. High signal to noise ratio (SNR) and spectral resolution observations are essential to validate our theoretical understanding of the non-LTE processes in the upper atmosphere, and to improve the available models, which still fail to quantitatively reproduce the observed emission spectra of terrestrial planets (Lopez-Valverde et al., 2011b). We here extend the analysis of the main characteristics of the 4.3 µm non-LTE emission to a large dataset of PFS limb observations. The final goal, beyond the scope of this paper, is to eventually build a retrieval algorithm to invert the radiances and determine important quantities like CO_2 abundance and non-LTE model collisional parameters, and to derive density and temperature variability of the upper mesosphere and lower thermosphere of Mars. So far, density variations at these altitudes are known with large uncertainties on Mars, the main information coming from model predictions rather than measurements. Some information has been obtained from aerobraking observations at a fixed local time (Theriot et al., 2006) and by the MEx ultraviolet spectrometer SPICAM (Forget et al., 2009; see Bertaux et al., 2006, for description of the SPICAM instrument). However, most data acquired by SPICAM were obtained at night-time, and the diurnal cycle could not be analyzed in detail.

In this paper we present the dataset and inspect the variability of the emerging radiance with respect to the parameters that mostly affect the spectral profile, i.e., altitude, solar zenith angle, season, latitude, local time, and thermal condition of the atmosphere. Kutepov et al. (2017) compared careful selections of PFS measurements to simulated spectra in order to improve non-LTE calculations, provide a more detailed description of the transitions and the non-LTE mechanisms responsible of the observed emissions, and constrain the development of accurate forward models. They showed that the long-standing discrepancy between observed and calculated spectra in the cores and wings of 4.3 µm region is explained by the non-thermal rotational distribution of molecules in the upper vibrational states 10011 and 10012 of the CO_2 main isotope second hot (SH) bands above 90 km altitude.

This paper will proceed as follows: in Section 2 we present the full dataset of PFS limb observations used in the present work. In Section 3 we describe and identify the main features observed in the PFS spectra at 4.3 µm. The variability of the emission with the tangent altitude is analyzed in Section 4, and the dependence of the non-LTE spectrum on the solar illumination is investigated in Section 5. In section 6 we discuss the variability of the intensity and the height of the peak emission