ESA Contract

Martian Environment Models

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WP6 Deliverable:

Non-LTE Effects in the Atmosphere of Mars.
A Technical Report

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Contents

Abstract

This report is an IAA contribution to WP6 of the ESA Contract Extension 11369/95/NL/JG CCN2, and reviews the current state of knowledge of the non-LTE situations that occur in the upper atmosphere of Mars and their potential impacts on the atmospheric radiative energy balance. We first recall basic concepts of non-LTE and the importance of this situation in the upper atmosphere of the terrestrial planets, and comment on the difficulties and limitations of current theoretical non-LTE models. Focus is kept on the characteristics of the non-LTE problem in the Mars' atmosphere. They are discussed, in particular, the role played by non-thermal processes and the complication of the non-linearities that arise from CO_2 hot transitions. Typical results of non-LTE populations and cooling rates by CO_2 emissions in the IR are also shown. A brief discussion about the need to develop parameterizations, like that for the current ESA contract under progress, is also presented.

1 Introduction

The study of Non-Local Thermodynamic Equilibrium (Non-LTE) situations has been linked to the development of the radiative transfer theory and to the description of the radiating properties of matter. The first treatment of non-LTE, for the study of stellar atmospheres, was by Milne (1931). Extensive studies of non-LTE have been carried out since then in order to interpret stellar spectra and stellar structure (Chandrasekhar, 1960; Mihalas, 1978). Regarding a planetary atmosphere, the first formulation of non-LTE was applied by Curtis and Goody (1956) in their analysis of the CO_2 15-μm cooling rate in the Earth's mesosphere.

Consideration of Non-LTE in the upper atmosphere is important, whenever it may be present, for a number of studies, like:
• calculations of atmospheric transmittances,
• analysis of radiances and spectra,
• remote sensing of atmospheric parameters, and
• evaluation of radiative cooling rates of the atmosphere.

This last application of non-LTE is of special relevance, since the radiative balance is the driving force of atmospheric circulations, and therefore, it can be very important for dynamical studies, particularly at high altitudes. The CCN2 extension of the above mentioned ESA project contemplates the extension in altitude of the GCM models used previously for the generation of the Martian Climate Database (see for example, Lewis et al [1999]), and therefore, a specific detailed study of non-LTE effects is required.

As a first step for such goal, we review in this Report the state of knowledge of the non-LTE effects in the Martian atmosphere, and present reference calculations for the validation of parameterizations under investigation. In particular, in the following sections we briefly review the nature of the non-LTE problem and their effects, the models developed so far to handle it in the Martian case, and the magnitude of its effects as obtained with the latest simulations.

2 Non-LTE in a Planetary Atmosphere

2.1 What is (Non-)LTE ?

In strict thermodynamic equilibrium, there is a unique parameter that determines the distribution of internal energy of a system, the temperature. In such case, both the translational energy and the internal energy of the system (rotational, vibrational, electronic, ...) are all described by well known functions of the temperature (and of some molecular parameters). These are the Maxwell and the Boltzmann distribution functions, respectively.

Such state would only be achieved in a closed and isolated system, like a gas inside a closed cavity with adiabatic walls. The radiation field inside the cavity would then also be known, since it is given by the Planck function at that temperature. The state of matter, and of the radiation field in the cavity, would therefore be completely known.

A planetary atmosphere is obviously not a closed and isolated system. It is not in thermodynamic equilibrium, showing important temperature changes from point to point and with time. Still, it is sometimes convenient to consider that, within some degree of approximation and in some regions or altitudes, i.e., locally, it is possible to describe its kinetic energy and its internal energy distribution functions by the equilibrium functions mentioned above using the local temperature as that single driving parameter. In such case we would still be able to know the state of matter. We call this a local thermodynamic equilibrium situation. It should be noted that the radiating properties of matter, i.e., the absorption coefficient, k_ν, and the source function for the transitions at work, J_ν, would depend solely on temperature, but the radiation field can be, however, quite different from the Planck function at the local temperature in an LTE situation, as will be shown below.

This is not the general situation. In a generic case, we have to study in detail each energy mode and try to describe it with appropriate distribution functions. We refer to this case as non-LTE.

We know that the translational energies rearrange faster than any internal energy mode, since it is a continuous function. The translational energy is found to be in equilibrium basically up to the exobase of any of the terrestrial planets. A kinetic temperature, T_K, can therefore be defined at each height of our interest. For the energy levels of the other modes it is usually possible to define a Boltzmann distribution, i.e., a function of some temperature. Then we can talk of "vibrational temperature", T_V, or "rotational temperature", T_R, etc, as the parameters employed in the Boltzmann distribution to describe the populations of the energy levels. If the vibrational temperature coincides with the local kinetic temperature, $T_V = T_K$, the vibrational levels are said to be in LTE. The state of matter would then be described completely if we are able to determine the distribution temperature for each internal energy mode, which is the purpose of the development of theoretical non-LTE models.

2.2 Modeling Non-LTE in a Planetary Atmosphere

The purpose of the non-LTE models is to determine under which conditions LTE holds and how to describe the state of the system when it does not. Non-LTE models have to consider all the microscopic processes that affect the populations of the excited levels. Atmospheric molecules exchange their excitation energy between the different energy modes and with the radiation field. In the terrestrial planets and in the infrared, the interactions of the atmospheric molecules with the radiation field mainly occur through three radiative processes: absorption, spontaneous emission and induced emission. On the other hand, exchanges of excitation energy with translational energy occur through *thermal collisional processes*. It is often necessary to consider also a large number of other processes usually referred to as *non-thermal processes*, like photochemical reactions, chemical recombination, electronic-to-vibrational and vibrational-to-vibrational energy transfers, charged particles collisions, etc... Therefore, non-LTE models basically consist in a number of *statistical equilibrium equations* (SEE) written for every excited energy level of interest and containing all the processes affecting that level population.

These equations are usually coupled among them and a simultaneous solution is required.

The resulting state from the competition among all theses different processes can be shown to be in LTE if the thermal collisions dominate. Collisional energy transfers are dependent on collisional cross sections and on the velocities of the colliding molecules, and if these velocities are in equilibrium, i.e., if there is a well defined kinetic temperature T_K, the resulting populations of the energy levels will also be in equilibrium, and at the same T_K. An LTE situation is therefore compatible with net gains or losses of radiant energy by the system, as far as these are small and do not perturb the thermal collisions' budget significantly. In an LTE state, when the gas absorption coefficient and source function are known, the radiation field (flux divergences and cooling rates) can be determined by solving the appropriate radiative transfer equation.

2.3 Difficulties and Limitations of Non-LTE Models

The non-LTE problem becomes specially complex when radiation-matter interactions are important. The populations of the excited states depend on the radiation field, and this in turn depends on the number density of the excited levels emitting at some resonant frequencies. Thus, the solution for the populations of the excited states, and for the cooling or heating produced by the radiative transitions, requires a completely self-consistent and simultaneous solution of both the radiative transfer and the statistical equilibrium equations for all energy levels and radiative transitions considered.

The number of equations to consider and to solve can be quite large if, as in the case of CO_2, the gas contains strong absorption bands and resonant energy levels with efficient energy transfer processes (see Section 3 below). Thus, the computational burden of a non-LTE model can be quite large. Some simplifications can be introduced once the behavior of the system is well established and understood, but in many cases the treatment of radiative transfer can not be fully avoided and the computational cost of the models is frequently very high.

The description of the non-LTE situations will be more complete the more comprehensive is the model used, i.e., the larger the number of processes incorporated. In practice, however, the knowledge of some energy transfer processes can be very incomplete, and a compromise between precision and simplicity of its treatment must be looked after. For example, there are many reaction rates not completely known yet, or with large discrepancies between determinations; also spectroscopic data have some degree of uncertainty, specially for hot transitions or for isotopic bands; and efficiencies for a number of energy transfers in non-thermal collisional processes may have never been measured in laboratory so far. Semi-empirical approximations for rate coefficients have to be employed in some cases, and sensitivity studies for those uncertainties are required in order to evaluate the impact of those uncertainties. For key processes the best solution is obviously to carry out dedicated laboratory experiments. The lack of this information can be the largest source of uncertainty for some non-LTE situations.

3 Non-LTE CO_2 Emissions in Mars

In this document we are concerned with the effects of the non-LTE situations in the Martian atmosphere on its radiative energy balance (cooling rates). This has been investigated by a very small number of works to date, since most non-LTE studies of the Martian atmosphere have been focussed so far on analysis of specific emissions, like the analysis of the CO_2 laser bands at 10-μm [Deming and Mumma, 1983; Gordiets and Panchenko, 1983], or the daylight enhancement of the 4.3-μm bands [Stepanova and Shved, 1985]. For that reason also, most of them introduced a number of simplifications (see Lopez-Valverde and Lopez-Puertas [1994a,b] for a short review). During nighttime the number of studies is even smaller, and all used important simplifications as well. The important 15-μm band system was studied in Mars and Venus by Ramanathan and Cess [1974] using an analytical broad band method, and by Bittner and Fricke [1987] and the groups at Arizona University and NCAR (Bougher and Dickinson [1988]; Bougher and Roble [1991]) with special emphasis on thermospheric seasonal and solar cycle variabilities. Possibly the most comprehensive non-LTE model for the Martian atmosphere so far is that developed by the group at the IAA in Granada [Lopez-Valverde, 1990; Lopez-Valverde and Lopez-Puertas, 1994a,b] (these works are referenced as Paper0, Paper1 and Paper2 hereandafter). They reproduced previous models' results and applied their model to the energy balance of the upper atmosphere [Lopez-Puertas and Lopez-Valverde, 1995] (this work is mentioned hereandafter as Paper3). They also used it in a first study of non-LTE effects on the thermal cooling and solar heating of the Martian upper atmosphere [Lopez-Valverde et al., 1998] (referenced as Paper4), and in the analysis of the Pathfinder entry profile [Lopez-Valverde et al, 1999] (Paper5). This is the model used for this ESA contract and for the results presented here.

Following all these results it seems clear that the strong CO_2 bands in the infrared give a very important contribution to the cooling and heating rates of the Martian atmosphere at all altitudes, and dominate the energy balance in the mesosphere and lower thermosphere. And that non-LTE effects can be very important in some conditions. Their accurate calculation is, therefore, necessary for any radiative or dynamical study extending up to those altitudes.

3.1 The CO_2 Vibration-Rotation Bands System

Since 95 % of the Martian atmosphere is composed of CO_2 and the other minor constituents with active IR transitions are present in very small abundances (specially in the upper atmosphere), CO_2 is the only gas that is needed for studying the radiative balance of the Martian mesosphere and lower thermosphere. In the IR, only rotational and vibrational transitions need to be considered, and the rotational ones can actually be considered in LTE up to the uppermost layer of the model (about 140 km for the non-LTE reference runs in the present ESA project) without important loss of accuracy. Therefore, only the vibrational distribution of levels is of our interest here.

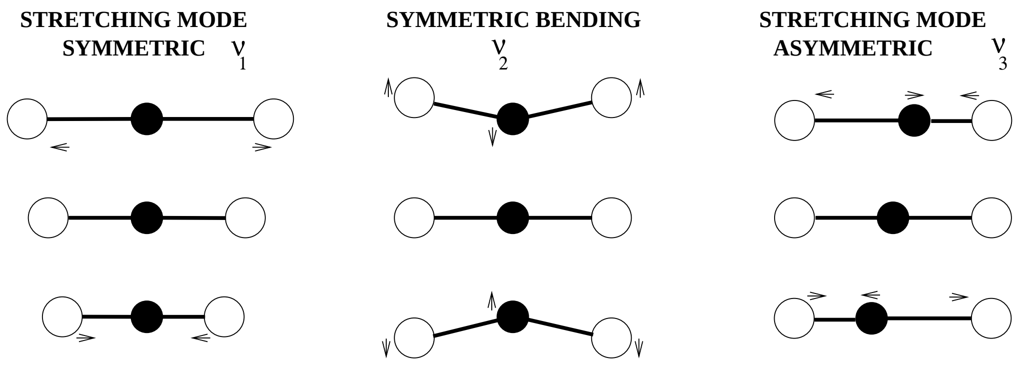

Figure 1: Schematic diagram of the three modes of vibration of the CO_2 molecule

This molecule possesses three vibrational modes, with transition energies of 1235, 667, and 2349 cm^{-1} (or 15, 7.6 and 4.3 μm bands). Figure 1 illustrates the three modes. The second of these, the bending mode or ν_2, is degenerate, very strong, and spectrally coincides with the maximum of a Planck function at typical Martian atmospheric temperatures. Figure 2 shows a schematic diagram of the most important radiative transitions between vibrational levels of the different modes of the main isotope of CO_2 in the IR. The bending levels are the most important system of transitions that produce a cooling of the Martian atmosphere, and are the subject of the parameterization study within this ESA contract. However, the excitation of the 15-μm levels by radiative relaxation of upper more energetic levels, as well as by collisional exchanges of excitation energy among CO_2 levels, makes it necessary to consider a very large number of CO_2 states of different isotopes. The number of transitions between all those levels amount to 92 in the current version of the non-LTE model, and are listed in Tables 1 and 2 in Paper1.

In a nearly pure CO_2 atmosphere there is a large variation of optical depths through the atmosphere which makes the transfer of radiation important for a large range of band strengths. This is an important complication compared with similar models of the Earth's atmosphere, for example.

3.2 Molecular Collisions in the Martian Atmosphere

Also the exchanges of vibrational energy between different modes and isotopes is very efficient in a CO_2 atmosphere. Consequently, a very complete scheme of vibrational-to-vibrational (V–V) collisional processes must be considered. The scheme included in the model was detailed in Table 3 of Paper1. Figure 3 shows a schematic diagram.

Some of these processes merit a small discussion. Among the V–T collisional processes, the most important excitation of the bending levels (0,ν_2,0) come from the atomic oxygen collisions: $CO_2(0,\nu_2,0)$ + $O(^3P)$ $\rightarrow CO_2(0,\nu_2-1,0)$ +

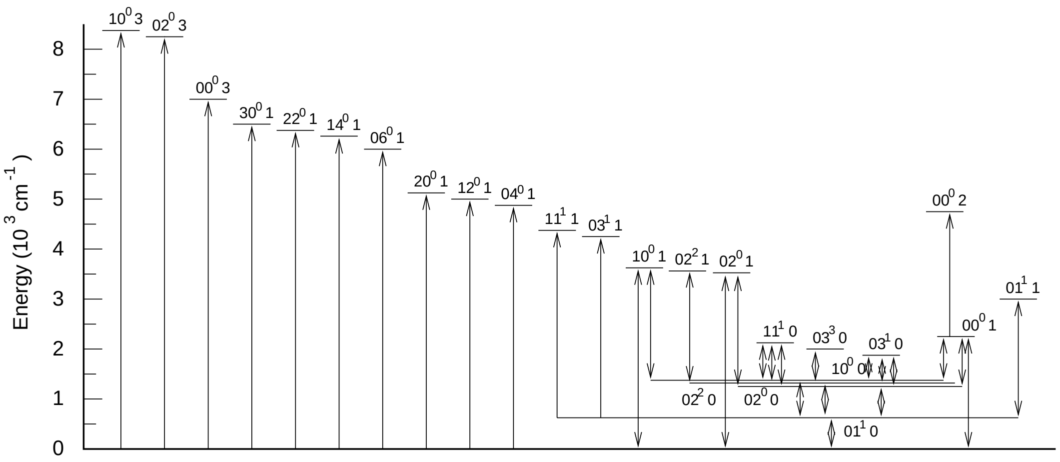

Figure 2: Vibrational levels and radiative transitions for the 626 isotope of CO_2 include in the non-LTE model. Double-ended arrows indicate vibrational-rotational bands studied including full radiative transfer.

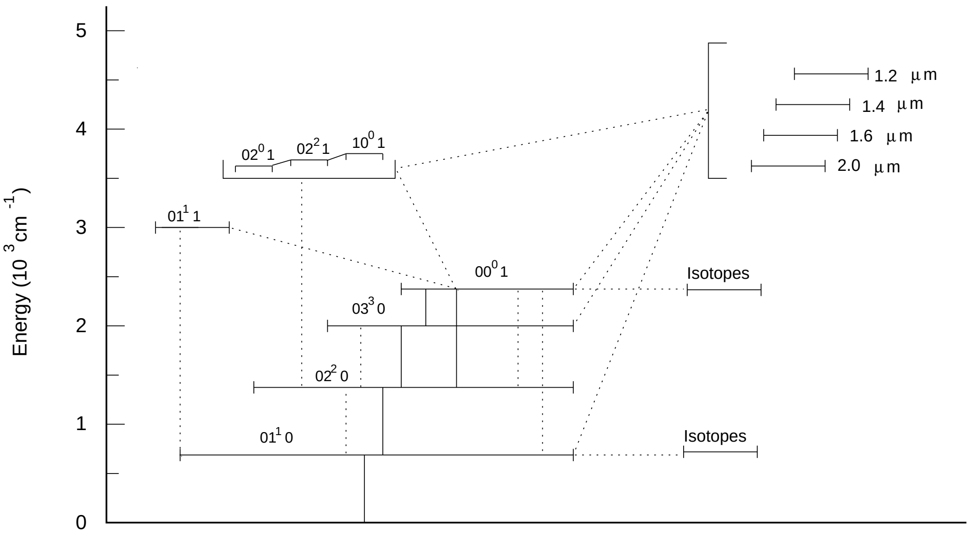

Figure 3: Schematic diagram of the collisional processes between the vibrational levels of the CO_2-626 isotope considered in the model. Vertical solid lines represent V–T collisions and dotted lines represent V–V exchanges. The high combinational levels' energies are not scaled.

O(^{3}P), with any excess energy released as kinetic energy of the colliding particles. The rate coefficient for this process had not been measured in laboratory until recently, and it was determined only at 300 K. The value used in the model, $k = 3 \times 10^{-12} cm^3 s^{-1}$, taken from Paper1, is in agreement with some indirect determinations from airglow and satellite occultation measurements of CO_2 15-μm radiances (Lopez-Puertas et al., 1992; see Paper1 for a more detailed discussion). The current uncertainty in this coefficient is about a factor 2.

By far the largest uncertainties in the collisional scheme of the model are due to V–V processes. Some of these are resonant energy transfers between CO_2 isotopes that exchange vibrational quanta within the same mode of vibration, and are therefore very efficient. The most relevant process for the vibrational temperature of the bending levels and the cooling rate at 15-μm is of the type $CO_2^i(0,\nu_2,0)$ + $CO_2^j(0,v_2,0)$ $\rightarrow CO_2^i(0,\nu_2-1,0)$ + $CO_2^j(0,v_2+1,0)$, where i, j would represent different CO_2 isotopes. Similar exchange reactions but for the asymmetric stretching mode, ν_3 are very important for the relaxation of high energetic CO_2 levels during daytime, after strong excitation by absorption of solar radiation in the near-IR (between 1 and 5 μm), i.e., for the solar heating. These rate coefficients have been measured at a couple of temperatures and only for the lowest vibrational levels. For higher overtone levels and minor isotopes it is necessary to make some assumptions (see Lopez-Valverde [1990] for a small review of some usual semi-empirical approximations). It has been customary to consider an order of magnitude as a conservative potential error estimate for these rates.

3.3 Radiative transfer

The exchange of photons between different atmospheric layers is a very important term for some of the most important non-LTE level populations of CO_2. This is the case of the first excited state of the bending mode (0,1,0), which is the responsible of the fundamental band at 15-μm. This band is not optically thin even in the Martian lower thermosphere. Other CO_2 transitions, however, are optically much thinner. This obvious result has important implications for the cooling rate of the Martian atmosphere. A large number of bands of different strengths can give significant contributions to the cooling of heating of that atmosphere at altitudes where the optically thick transitions can not produce efficient coolings. Typical results are commented below. All this has to be taken into account for the calculation of non-LTE populations and the cooling rates associated.

This situation is actually common to LTE calculations. Special complications (non-linearities) in the calculation of radiation transfer appear in non-LTE conditions. The first one occurs when hot bands become optically thick. The lower levels of these transitions are not the ground state, and in non-LTE their populations need to be determined in order to correct for the absorption coefficient. Not only their SEE equations must be solved simultaneously with the radiative transfer equation of the transition at work, but also an iterative procedure is later necessary to avoid the non-linearity. The first hot bands of the major isotope is a good example of this case, which present important reabsorptions in the Martian mesosphere, specially during daytime conditions (Paper2).

In addition, collisional processes can interact and modify the radiative transfer peculiarities of the Martian mesosphere and lower thermosphere. For example, in the absence of V–V collisions among different isotopes the (0,1,0) level of the minor isotopes would radiate and cool the atmosphere in a small amount by *emission-to-space*. However, the strong collisional coupling between the bending levels of the different CO_2 isotopes enhances the cooling rate in the mesosphere (Paper3). When collisions lose importance in the upper layers, the isotopic levels are much less populated and their emissions cool the atmosphere at a much smaller rate than a LTE calculation would suggest. This is why non-LTE cooling rates are usually smaller than in LTE (Paper4).

Also radiation exchanges between atmospheric layers compete with collisional processes when energy is directly absorbed from the solar flux in the near-IR. Before this energy can be thermalized some fraction could be emitted to space, reducing the potential solar heating of the atmosphere (see Paper3). This is why non-LTE solar heating is always smaller than LTE calculations show (Paper4).

4 Non-LTE Effects in the Martian Atmosphere

We have just discussed that in non-LTE situations the thermal cooling and the solar heating of the Martian atmosphere are usually smaller than in LTE. In this section we show quantitative estimates and examples.

4.1 Vibrational Excitations of the CO_2 States

The atmospheric parameters affected by non-LTE which are most directly subject to verification by measurements are the populations of the vibrational levels. These can be sounded from remote observations by detecting their IR emissions. An example is the instrument PMIRR, on board the failed missions Mars Observer and Mars Climate Orbiter, which was planned to derive the thermal structure of the Martian atmosphere by sounding the 15-μm CO_2 bands (McCleese et al., 1992). To describe the populations of the levels, instead of number densities it is more frequent to use the concept of vibrational temperature. For a particular vibrational level u it is defined as

$$T_V = \frac{E_u}{k \ln(\frac{n_u g_0}{n_0 g_u})}$$

where E_u, n_u, and g_u are its energy, number density, and degeneracy and n_0 and g_0 refer to the ground level. This quantity permits a direct comparison with the LTE case, which corresponds to $T_V = T_K$.

The vibrational populations, or temperatures, of a large number of CO_2 states have been presented for nighttime and daytime conditions in Paper1 and Paper2 respectively. Figure 4 shows a calculation for the bending levels of a number of isotopes for a particular reference model atmosphere at night. This model atmosphere has been compiled for this ESA project (see Section 5 below). During nighttime the departure from LTE in the 15-μm bending levels occur around 90 or 100 km, and is due to spontaneous emission to space. The populations are usually smaller than the LTE case (vibrational temperatures smaller than the kinetic one) and tend to constant values at the top of the atmosphere (see Paper4 for more details).

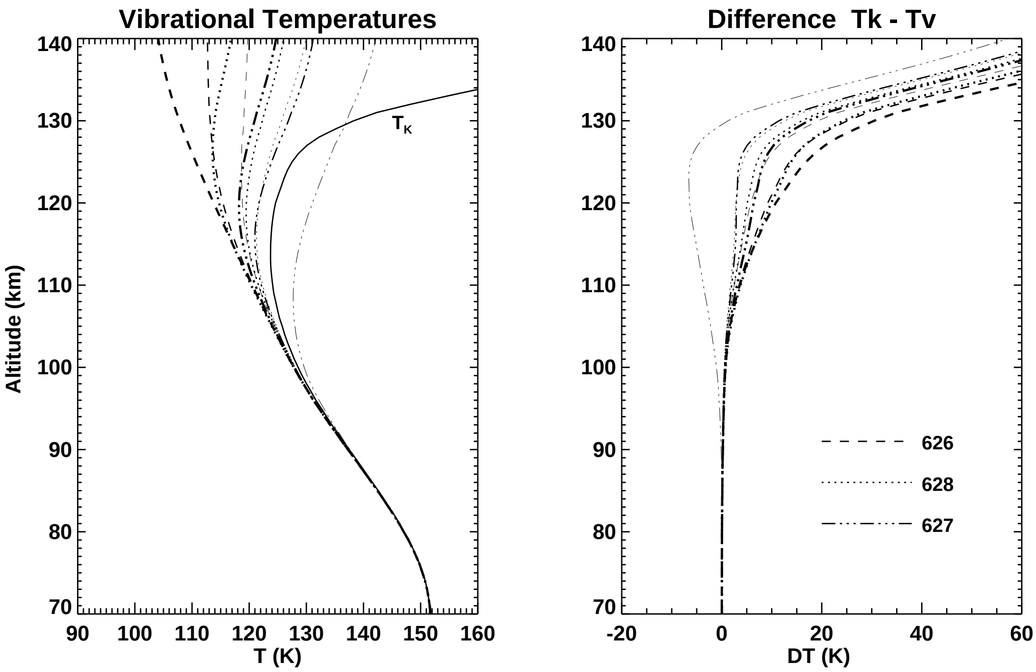

Figure 4: Vibrational temperatures of bending levels of CO_2 isotopes for the Martian reference model atmosphere #1 (see text). Thin lines: levels (0,3,0); thick: (0,2,0) levels; very thick: (0,1,0) levels. Line-styles represent different isotopes, as indicated.

During daytime the CO_2 levels with excitation in their ν_3 quanta, like the fundamental band at 4.3-μm, show very large populations above about 40 km. This is a consequence of the direct absorption of solar radiation in those bands. Also the 2.7-μm levels reach very high values in the mesosphere and thermosphere. That altitude of LTE breakdown varies for different CO_2 levels, and can be even much lower for very weak high combination bands, which are optically thin and can penetrate to very deep atmospheric layers. All these levels can relax their excitation by spontaneous emission to space or by collisional deactivation, ending up as lower energy CO_2 levels. These relaxation mechanisms are important sources of excitation of the lower 15-μm levels, which do not present direct solar absorptions but do have much stronger emissions during daytime for this mechanism. In fact they can have populations larger than the LTE ones in some altitude range of the upper mesosphere (90-120 km), in clear contrast to nighttime conditions (see Paper2).

4.2 Thermal Cooling Rates

The usual effect of non-LTE on the cooling rates at 15-μm is, as mentioned above, to reduce them. This is because the number density of the emitting levels is smaller when the spontaneous emission to space competes with vibrational-thermal collisions (V–T). This occurs around 100 km in the Martian atmosphere. However, due to radiative transfer, the actual temperature structure at altitudes one or two scale heights away from this layer can have profound effects on the cooling (Paper4).

It is important to note also that during daytime the emission at 15-μm is much larger than at night. This enhanced emission is, however, of solar origin and does not originate from kinetic energy of the atmosphere (through V–T collisions). It is only a fraction of that large daylight emission what will actually correspond to this V–T source and what will amount to a real atmospheric cooling (Paper3).

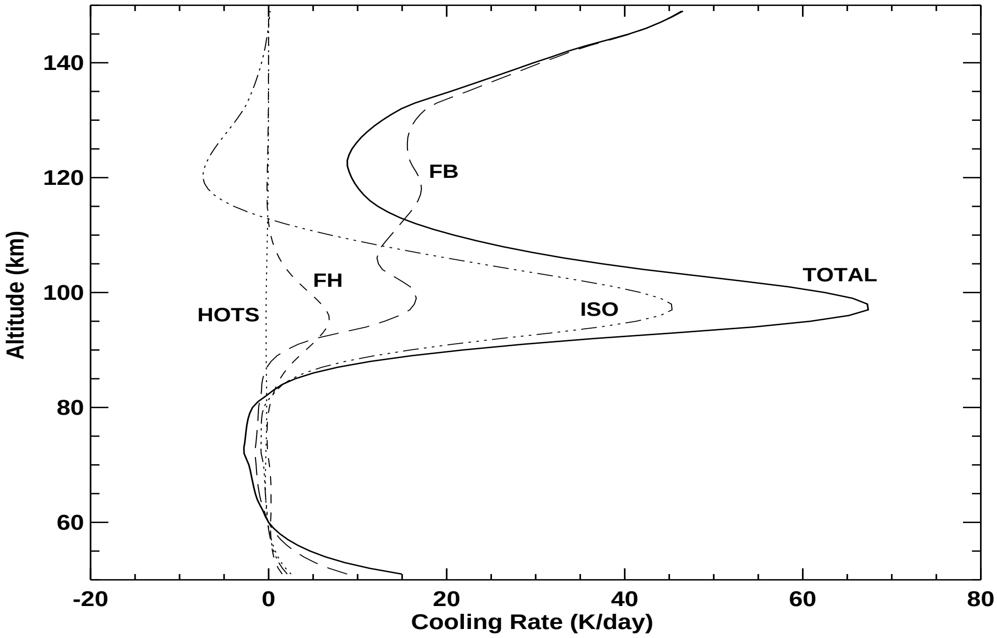

Figure 5: Cooling rates of the 15-μm CO_2 bands, as indicated, for the Martian reference model atmosphere #1 (see text). FB and FH: Fundamental and First Hot bands of the main isotope; ISO: sum of the fundamental bands of the 636, 628 and 627 isotopes; HOTS: contribution from remaining hot bands in the model; TOTAL: sum of all the contributions.

Figure 5 shows the cooling rates due to the most important 15-μm bands in a calculation for the same reference atmosphere as in Figure 4. Depending on how an LTE calculation is defined (up to which altitude) the discrepancy with the non-LTE case will vary. Usually the effect is small at all altitudes below one scale height of the top layer if the LTE calculation is kept within the LTE region (below 95 or 100 km in this case). However, an LTE run extended in altitude above the LTE breakdown layer can produce extremely large errors, even in the LTE region (see Paper4 for some examples).

We observe in Figure 5 a large contribution from the fundamental band of the main isotope (626-FB) in the upper layers, while the weaker bands of the minor isotopes or the first hot of the 626 isotope are more effective coolers of the Martian mesosphere at lower altitudes. This is a general feature for any reference model of the Martian mesosphere. However, the absolute values of the cooling rates are very dependent on the thermal structure of the atmosphere and on the speed of the collisional V-T processes. In the upper atmosphere of Mars the collisions dominating the cooling are those between CO_2 and atomic oxygen, and a detailed knowledge of the abundance and distribution of this minor constituent is necessary, as well as a good knowledge of its energy transfer rate coefficient. The current uncertainty in this rate, about a factor 2, is similar to the variability in $O(^3P)$ abundances that can be deduced from composition models (Rodrigo et al. [1990], Moreau et al. [1991], Nier et al. [1994]).

Let us recall that cooling rate calculations are very expensive because the bands responsible for the most important emissions are optically thick and no simple approximations are appropriate at all altitudes. A common approach is the *cool-to-space*, which is usually very appropriate in the very high atmosphere, when the bands are optically thin. This is, however, not the case for the 626-FB below about 130 km, which is the region of our interest. Thus, in general radiative transfer has to be solved among many atmospheric layers, and in non-LTE, coupled with the statistical equilibrium equations of all the CO_2 levels involved. Another simple approximation to avoid non-LTE complications is to replace the thermosphere with an LTE buffer region at the top of the mesosphere. This can work for a benchmark case, but it is difficult to export generalities applicable to different cases, given the large dependence of the cooling rate on the local thermal structure and the usual thermospheric variation of the source function (see Paper4 for more details).

4.3 Solar Heating Rates

The absorption of solar radiation by the atmospheric molecules produces heating of the gas. In LTE this magnitude can be directly computed from the absorption coefficient of the absorbing gas and the incident solar flux. All these can be known to high accuracy. However, in a non-LTE situation like the daylight atmosphere of Mars above 40 km, not all the incident solar radiation that is absorbed ends up as atmospheric heating, but only a fraction. Let us recall again that the non-LTE solar heating is a fraction of the LTE one. The reason was mentioned above: the energy taken from the solar flux is momentarily stored as excitation energy of the CO_2 vibrational state associated with the transition of interest before it can be released to the atmospheric molecules as kinetic energy (through V–T collisional processes). If V–T collisions are not very frequent enough, and this is the case in all upper atmospheres, the energy may be re-emitted back to space at the same frequencies, or lost to other vibrational levels by non-thermal collisions (V–V). Those other levels may in turn posses optically thin transitions and be able to emit another fraction to space. Eventually, the total fraction of the initial solar absorption that is finally thermalized can be very small above some altitude, like 140 km in Mars. An LTE solar heating would be in very large errors at those altitudes. On the contrary, below about 60 km most of the solar absorption is effectively thermalized, and the LTE solar heating is basically correct. The error in the solar heating due to the LTE assumption was studied in Paper4.

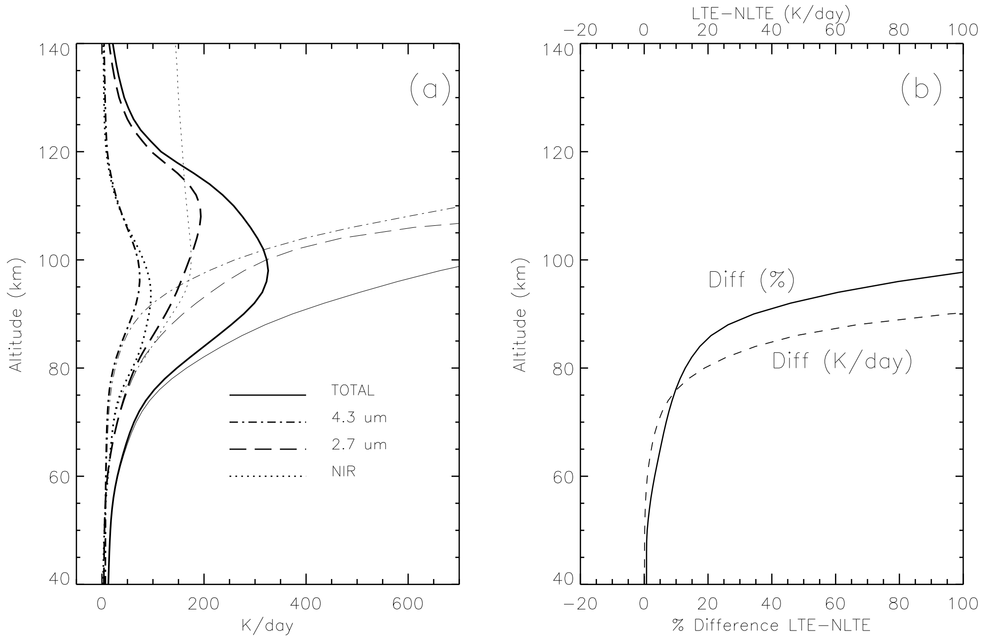

Figure 6: Solar heating rates in three CO_2 band systems in the near-IR, as indicated, and for sun overhead conditions. Thick lines: non-LTE; thin lines: LTE

Figure 6 shows an example of LTE versus non-LTE solar heating rates for a particular reference atmosphere and non-LTE parameters. The solar heating from the most important CO_2 bands in three spectral regions are shown in the figure for sun-overhead conditions. They all increase steadily with altitude in the lower mesosphere (60-90 km) as the direct solar absorption becomes larger. However, above about 100 km the non-LTE solar heating start decreasing with altitude, in contrast to the LTE expectations, as the collisional V–T deactivation becomes less and less efficient.

5 Parameterization of Non-LTE Effects

Running a non-LTE code on-line in order to compute thermal cooling and solar heating rates is completely impractical, as explained above. A number of acceleration methods have been investigated in the past for similar problems in the Earths atmosphere. These have included simplifications of both the statistical equilibrium equations and the radiative transfer equations. The most expensive part certainly comes from the radiative transfer in those vibration-rotation bands which are very optically thick in the lowest altitudes of interest and very optically thin in the upper range. Regarding the simplifications to radiative transfer, one of the more common ones is the cool-to-space, mentioned above, which eliminates contributions to and from other atmospheric layers and considers only the exchange term with the upper boundary. This has been used extensively in the past, specially when no other alternative was available. This is the case of the Thermospheric Martian GCM developed at NCAR (Bougher et al. [1986]). However this is not a good approximation below about 125 km for the 626-FB, which is the largest contribution to the total cooling rate at this height. Parameterizations of radiative transfer are among the fastest methods, but there are no available studies so far for the Martian upper atmosphere. Their accuracy must be tested against accurate computations. One of the objectives of the present ESA contract is the development of a parameterization of the cooling rates at 15-μm. We expect to report on the current studies and the progresses achieved in this direction soon (by the end of the project).

The solar heating counterpart is more computationally expensive than the thermal cooling in a normal non-LTE calculation, but fortunately its weak dependence on the thermal structure of the atmosphere makes it more suitable to tabulations, as discussed in Paper4. In this work, the authors proposed a table of correcting factors as a function of pressure only. This simple tabulation is subject to some degree of uncertainty due to variations in solar zenith angle and to V–V rate coefficients uncertainties. It should be revisited and extended in a future, but at present it represents the best correction for non-LTE in the solar heating, and has been already incorporated in the LMD and Oxford GCMs [Forget et al., 1999].

At the moment of writing up the present Report, a number of eight reference thermal profiles for the Martian atmosphere has been set up to serve as a benchmark for the development and validation of a parameterization for the 15-μm cooling rates. The profiles are shown in Figure 7. Four of the reference profiles correspond to outputs of the GCM used to compile the Martian Database, for different latitudes and Martian seasons and solar illuminations. The four remaining profiles correspond to Viking 1, to Pathfinder conditions, and to two radiative equilibrium calculations (night and daytime) obtained running the IAA 1-D non-LTE radiative model in a time-marching fashion. Overall, these reference calculations cover widely diverse and realistic scenarios, with diverse cooling rates, as shown in Figure 8.

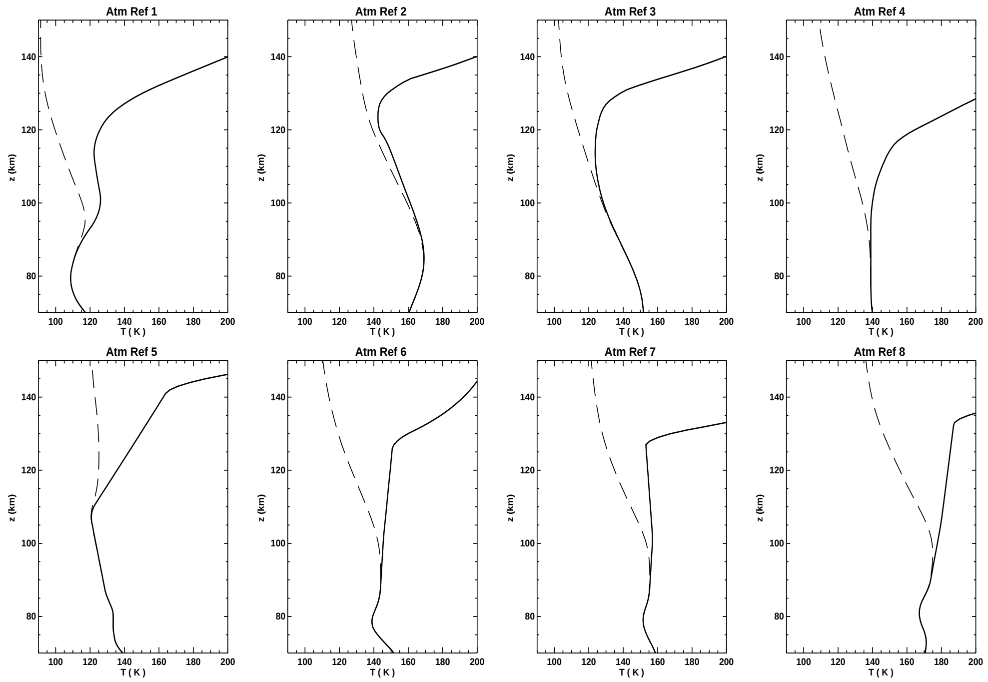

Figure 7: Set of eight reference temperature profiles of the Martian atmosphere. Solid line: T_K; dashed line: nighttime vibrational temperature of the 010-626 level.

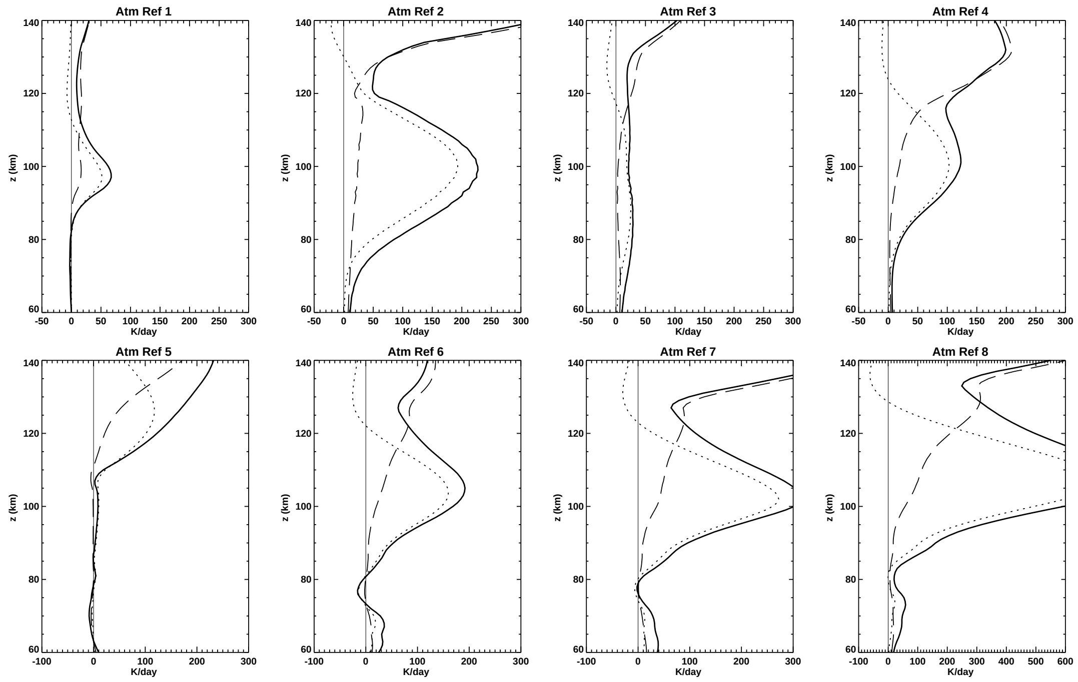

Figure 8: Cooling rates by the CO_2 15-μm bands in the Martian atmosphere for the set of reference temperature profiles shown in Figure 7. Dashed line: contribution from the 626 fundamental band; dotted line: sum of the isotopic fundamental and 626 first hot bands; thick solid line: total cooling rate.

6 Summary

Current knowledge of CO_2 non-LTE situations in the Martian atmosphere are reviewed. These situations normally occur in the upper atmosphere, where collisional V–T processes become less efficient as the dominant excitation processes of the molecular vibrational levels of interest, CO_2 in our case. This situations affect the CO_2 IR emissions and the remote sounding of atmospheric temperature and pressure. The associated thermal cooling and solar heating rates can also be severely modified, and dedicated non-LTE models are required for their calculation. These models usually solve a number of statistical equilibrium equations for each vibrational level of interest, including all microscopic processes (collisional, radiative, photochemical, etc...) able to populate or deactivate that excited state. When radiative transfer is important, the statistical equations must be properly coupled to radiative transfer equations, and all of them solved simultaneously. Non-linearities, which can arise from non-thermal processes (like V–V collisions) or from radiative absorptions in hot transitions, complicate the solution, which must follow a suitable iterative scheme. The total number of levels and bands in a CO_2 atmosphere like the Martian case is very large if a comprehensive scheme of energy exchanges via collisions and radiative transitions is sought (see Figures 2 and 3). Non-LTE models for CO_2 emissions in the Mars' atmosphere are, therefore, computational expensive.

The departure from LTE in the bending levels of CO_2, responsible for the strong 15-μm emissions, starts around 90 km, showing deviations of varying magnitude depending mainly on the thermal structure of the upper mesosphere and lower thermosphere. The populations of all 15-μm levels in the non-LTE region are smaller than their equilibrium values during nighttime, although they may present local enhancements during the day due to relaxation of high energy CO_2 levels, which are excited by solar absorption in the near-IR. The cooling rate at 15-μm usually presents a local peak around 100 km, due to the fundamental bands of the minor isotopes and to the first hot band of the 626 isotope, and another maximum well into the thermosphere, where the 626 fundamental band becomes optically thin. The cooling rates depend strongly on the thermal structure and on V–T collisions between CO_2 and atomic oxygen. The current variability of atomic oxygen abundances and the uncertainty in the rate coefficient for V–T transfer are estimated as a factor 2 approximately.

A very small number of approximations have been applied to the non-LTE regime in the Martian atmosphere. That of Bougher et al. [1986] for the Thermospheric Martian GCM is based on the cooling-to-space approximation, which we have proved to be incorrect below about 125 km (Paper3). The on-going development of our new parameterization for the Martian upper atmosphere intends to improve on the actual situation. It will be based on and validated against a set of reference non-LTE calculations presented in Figures 7 and 8.

Regarding the solar heating rates in non-LTE conditions, these do present important differences in the upper atmosphere with any LTE approximation, due to the overestimation that this approximation makes of the thermalization of the initial solar absorption. Thermalization requires V–T collisional deactivation, which is a very slow process at the low densities of the upper Martian atmosphere. Consequently, also the real solar heating is smaller than what LTE presumes. The dependence of the solar heating on the thermal structure of the atmosphere is, however, much weaker than the cooling rates, and this makes possible some fast approaches to its proper inclusion in large models like a GCM. At present, tabulations like that of Lopez-Valverde et al. [1998] can be employed in GCMs until they are updated or extended in a future (Haberle et al. [1999], Forget et al. [1999]).

Overall, there is a number of uncertainties in our current description of the non-LTE situations in Mars, the largest one deriving from incomplete knowledge of some rate coefficients. Also inaccuracies in radiative transfer or lack of consideration of potential excitation processes in the models can not be ruled out. In this regard, the lack of proper observational data from the upper atmosphere of Mars is a severe drawback for any non-LTE model. Again this recalls the unfortunate loss of PMIRR and the Mars Climate Orbiter, one of the few instruments planned nowadays with potential insights into the mesosphere of Mars and its non-LTE behavior.

7 References

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