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DEFINITION OF A NEW LEVEL ONE TEST CASE – MEASUREMENTS OF EQUILIBRIUM RADIATION FROM AN INDUCTIVELY COUPLED PLASMA IN THE NEAR–UV TO NEAR–IR SPECTRAL REGION FOR A MARTIAN–TYPE CO_2–N_2 MIXTURE

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ABSTRACT

A new test case, using a quasi-similar methodology and experimental set-up than previous test case 1, is presented in this paper. An inductively coupled plasma torch, working at atmospheric pressure, is used to create CO_2–N_2 Martian-like plasma (97% CO_2–3% N_2). The operating frequency and power are 64 MHz and 3 kW respectively. This kind of apparatus allows obtaining plasma in chemical and quasi-thermal equilibrium. The plasma characterization will consist firstly to determining the chemical composition; a calculation code based on the Gibbs free energy minimization is used. Secondly, the radial temperature profiles will be given through Abel inversion of atomic and molecular systems. The spectral measurements cover the [250–800] nm range and are performed inside the induction coil. Each interesting spectrum is Abel-inverted and calibrated in order to determine the volumetric emission coefficient. These spectra are then compared to the line-by-line spectral code SESAM used for the simulation of the radiative emission of entry-type plasma.

1. INTRODUCTION

Different levels of test-cases have been defined in the frame of the radiation working group. Such test-cases are useful for the evaluation and validation of radiation models used for atmospheric entry applications.

Test case n° 1 is devoted to the validation of models of line-by-line spectroscopic codes and of spectral data used for line-by-line radiation calculations. As the simplest case is the modelling of plasma in thermo-chemical equilibrium, an ICP torch, which allows obtaining such conditions, is used. Test case 1 was initially intended to validate measurements in air plasma (Laux 1993). This new level of test case 1 proposes a spectroscopic study of plasma formed with a Martian-like atmosphere gas mixture, which will be useful for the validation of spectral databases likely to be used for Martian-type entries radiation simulations (SESAM code).

The outline of the paper is as follows. In section 2, all the characteristics of the experimental set-up and the calibration process are given. In section 3, experimental spectra in the range [250-800] nm are presented. In section 4, we discuss about the validity concerning the thermal and chemical equilibrium assumptions. On one hand, thermal equilibrium is considered by comparison between experimental and numerical spectra. On the other hand, the determination of the reaction rates leads us to say that chemical equilibrium is reached under our experimental conditions. Then, the chemical composition of a CO_2–N_2 Martian-like plasma (97% CO_2–3% N_2) is given through the calculation code based on the Gibbs free energy minimization.

2. EXPERIMENTAL SET-UP

2.1. Main characteristics

The ICP-T64 torch located at the L.A.E.P.T. (Thermal Plasmas and Electrical Arc Laboratory) in Clermont-Ferrand, France, is a classical ICP torch able to work with different kinds of plasma gas (air, argon, CO_2, N_2 and gas mixtures). This inductively coupled plasma system operates at a frequency of 64 MHz. A seven-turn induction coil, cooled by air, is used to ignite and sustain the CO_2–N_2 plasma. It can be noted that the use of a seven turn induction coil modify significantly the plasma aspect compared with that one with a classical five turn. We observed a brighter needle along the axis. A first explanation concerns the fact that the discharge is not only inductive but there's also a capacitive effect, involving an axial component of the electric field. A second one concerns the consideration of the skin effect, which can be different according to the gas used to form the plasma. So, in our case, the analytical zone is relatively weak, near the plasma axis.

The main features of the experimental set-up and operating conditions are reported in Fig. 1 and Tab. 1, respectively. The plasma is generated through the induction coil by a radio frequency (RF) of 64 MHz delivering a power up to 3 kW. The plasma is confined within a 28 mm

quartz tube. The plasma gas is injected at a fixed rate of 6.6 L/min (In order to have a mixture of 97% CO_2–3% N_2 in molar proportion, the CO_2 and N_2 flow rate is 6.4 and 0.2 L/min respectively).
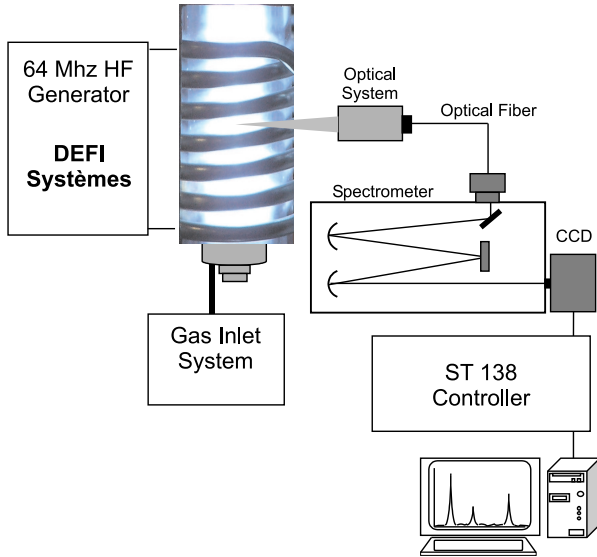

Figure 1. Plasma torch and detection experimental set-up

Inductively coupled plasma	
Manufacturer/type:	Défi Systèmes/ICP T64
Power supply:	64 MHz, 3 kW
Tuning:	Automatic adaptation
Inductor:	Seven-turn air-cooled coil
Plasma gas flow rate:	6.6 L/min
Operating pressure:	atmospheric pressure
Torch:	28 mm internal diameter quartz tube
Optical set-up	
Spectrometer:	Chromex ST 138
	500 mm focal length
	Czerny-turner mounting
Entrance slit:	e = 100 µm
Gratings:	1800 grooves/mm
Detector:	CCD EEV 1152x1242 pixels
Spatial resolution:	1 mm
Apparatus function:	0.08 nm

Table 1. Main features of the experimental set-up

The optical set-up, placed at 34.3 cm from the plasma axis, leads to a spatial resolution of 1mm. Spectral lines intensities are measured with a 0.50 m focal length Czerny-Turner monochromator connected to a CCD detector (1242x1152 pixels, each pixel having a width of 22.5 µm). An 1800 grooves/mm grating is used. Its apparatus function $\Delta\lambda_{app}$, assimilated to a Gaussian profile with a full width at half maximum, is calculated from the relation

$$\Delta\lambda_{app} = FWHM \cdot f_p \cdot D^{-1} \tag{1}$$

where $FWHM$ is expressed in pixels, D^{-1} represents

the gratings dispersion (1.025 nm/mm) and f_p defines the pixel dimension (22.5 µm). The calculated value of gives 0.08 nm for an entrance slit equal to 100 µm.

2.2. Intensity calibration

The measured emission spectra must be corrected from the spectral response of the optical device, which include lens, monochromator and CCD detector. So, a calibration in intensity, between 250 and 800 nm, is necessary to take into account all these effects. A Deuterium lamp (HAMAMATSU L1626 30 W) and a tungsten lamp (OS-RAM WI14) are used to cover the range [200-400] nm and [300-800] nm respectively.

The calibration procedure is realized in the same conditions that ones considered for the experimental spectral acquisitions. The spectral radiance of the two calibration lamps are reported on Fig. 2; Fig. 3 represents the spectral response of the optical system. The problem of the chromatic aberration is not considered in this paper as a calculation shows that it is inferior to the spatial resolution of the optical set. Fig. 4 reports the influence of the chromatic aberration as a function of wavelength. It can be seen that it becomes significant at wavelengths near 300 nm.
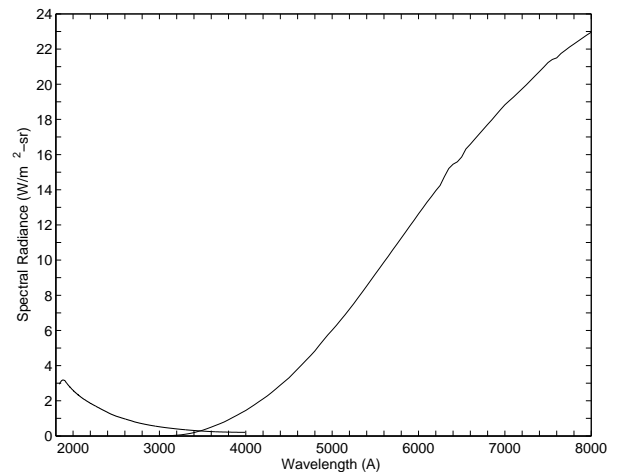

Figure 2. Spectral radiance of the Tungsten and Deuterium calibration lamps

3. EXPERIMENTAL SPECTRUM

Optical emission spectroscopy is the simplest non-intrusive method for plasma diagnostics. The analytical zone is limited between the fourth and the fifth induction coil where the luminous response is the greatest. Each spectrum corresponds to one acquisition of one second and the electronic noise is automatically subtracted. Fig. 5 reports a global spectrum recording from the plasma formed with a Martian-like atmosphere in the
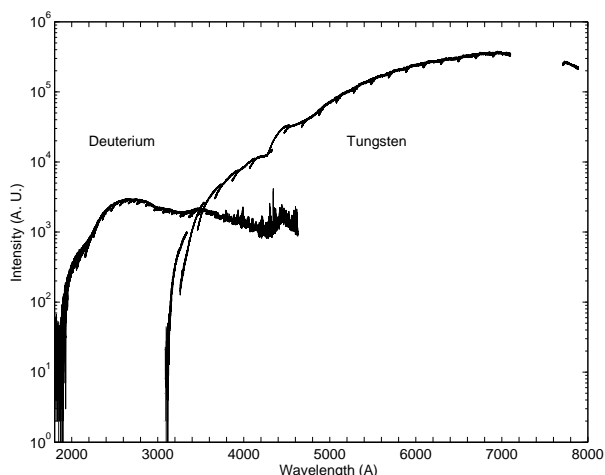
Figure 3. Spectral response of the optical system for the Tungsten and Deuterium calibration lamps
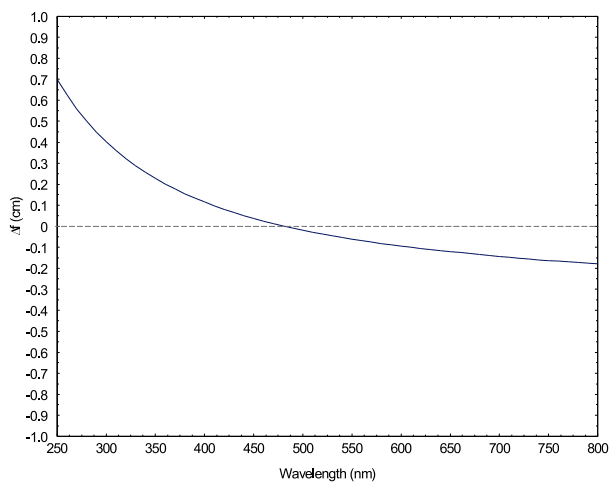

Figure 4. Variation of the focal distance as a function of wavelength, with a quartz lens

range [250–720] nm. The CN molecular emission is predominant whereas the C_2 emission is relatively weak. We can also observe an atomic line of carbon in the near UV at 248 nm. Measurements up to 900 nm can be carried with the optical apparatus, but a problem with the ICP facility prevented such measurements to be completed in the [720–900] nm spectral range. The measured spectra was Abel inverted and calibrated in intensity in order to obtain the volumetric emission coefficient of each interesting wavelength.

A special attention must be made on the application of the Abel inversion in ICP torch. The curvature of the quartz cylinder can play a non-negligible role in the radial spectral acquisitions. For our experimental conditions, by geometric considerations, the signal received by the optical device does no longer correspond to the position concerned inside the plasma when the radial position of the optical fibre is above 7 mm. In our case, as the analytical zone is restricted to 2–2.5 mm around the plasma axis, the Abel inversion can be done without errors.
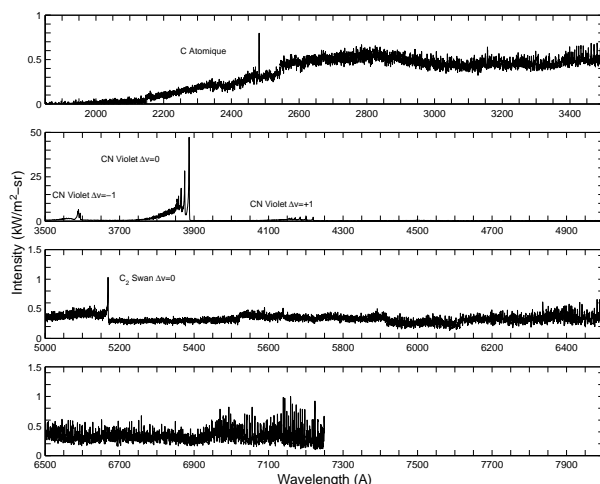

Figure 5. Emission from the CO_2-N_2 plasma inside the induction coil of the torch

Fig. 6 represents different intensity radial evolutions of CN peaks and Fig. 7 shows the result of the application of Abel inversion for a particular wavelength. It must be noted that each intensity radial evolution of wavelength is interpolated by cubic splines and fitted by a polynomial of degree 9 before applying the Abel inversion.
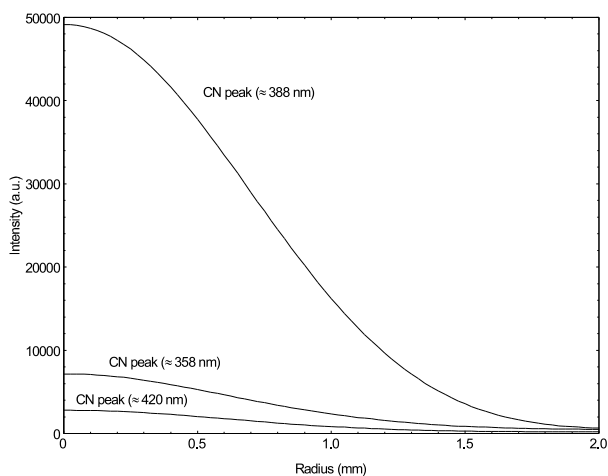

Figure 6. Radial evolution of intensity peaks of the CN bands

4. THERMODYNAMICAL EQUILIBRIUM

Inductively coupled plasma working at atmospheric pressure can generally be considered in thermodynamical equilibrium. Depending of the type of gas and the torch power, a little departure from thermal equilibrium can be observed in such plasmas. It is the case for air plasmas where a factor of 1.1 to 1.2 exists between the electronic and the heavy particle temperatures. It will be shown from experimental spectra and numerical ones that thermal equilibrium is reach under our experimental conditions. The problem of the chemical equilibrium
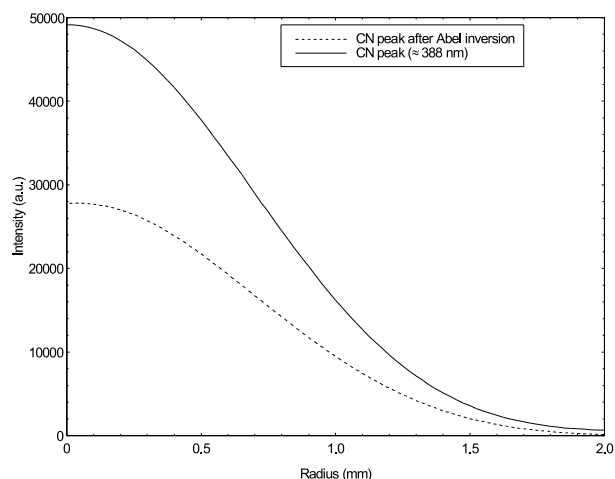
Figure 7. Example of the Abel inversion application on an CN peak (≈ 388 nm)

is also investigated in order to confirm the possibility to make spectral acquisitions inside the induction coil of the plasma torch.

Spectral acquisitions being performed between the fourth and the fifth coil of the inductor, we have to be sure that chemical equilibrium is reached at this point.

A first needed step is the calculation of the flow residence time. The distance between two successive inductor coils is 4 mm wide. The mass flow $\dot{m}$ is held fixed, and the density ρ remains equivalent to the density at room temperature, as the flow transits at a constant volume rate inside the quartz tube. Taking into account the mass continuity relationship:

$$\dot{m} = \rho A v \tag{2}$$

the flow velocity can be determined, and the flow residence time from the inductor base to the point considered previously, corresponds to 0.12 s. The residence time between the 4th and 5th coil is therefore 30 ms.

4.1. Thermal equilibrium

The SESAM code (Lino da Silva 2004) has been used to reproduce the Abel-inverted CN spectra obtained along the plasma radius. The distribution of the rotational and vibrational levels of the simulated spectra was iterated until a best fit with the experimental spectra was obtained. The rotational and vibrational levels were found to follow a Boltzmann distribution and to be in equilibrium ($T_{vib}=T_{rot}$) along the overall radial range where emission of the plasma was recorded (0-2.5 mm). An example of the fit of the abel-inverted and simulated spectra is presented in Fig. 8 for the CN Violet system $\Delta v = 0, -1$ transitions.

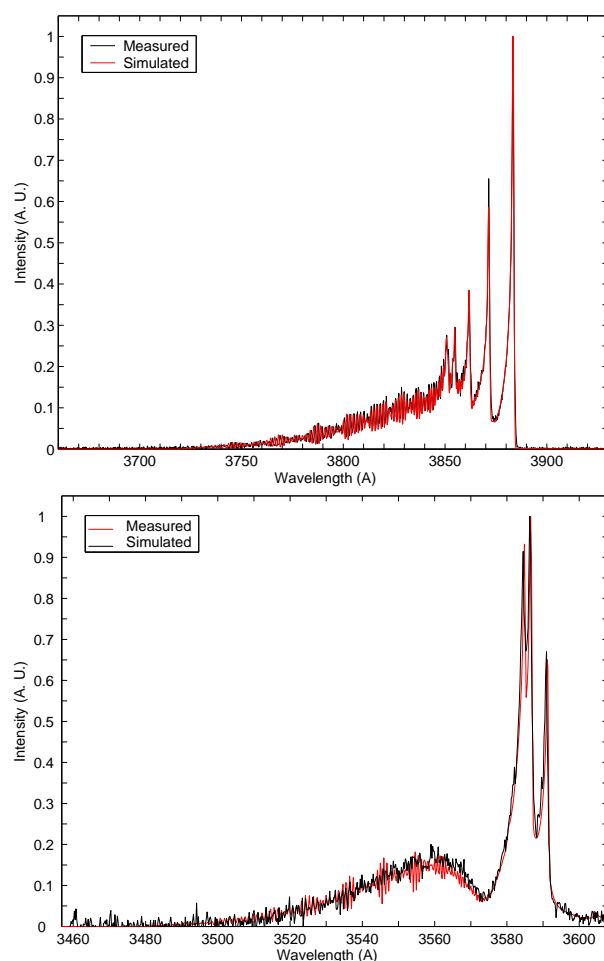It is therefore assumed that the plasma can be described through the use of one overall temperature T. The radial

Figure 8. Simulation of the radiative emission of the CN Violet system over the ICP torch axis (r=0) for the $\Delta v = 0$ (top) and $\Delta v = -1$ (bottom) transitions

temperature profile, determined through the fit of the CN Violet system measured spectra using the SESAM code, is presented in Tab. 2

Radial Distance (mm)	Temperature (K)
0.0	6050 ± 50
0.5	6050 ± 50
1.0	6050 ± 50
1.5	5900 ± 100
2.0	5900 ± 1000

Table 2. Radial temperature profile of the plasma

It would be interesting to complete these temperature profile measurements by some temperature measurements through the measurement of atomic line peaks. This allows obtaining the excitation temperature T_{exc} of the transition electronic levels, and this temperature should be compared to the vibrational T_{vib} and rotational temperatures T_{rot} of the CN Violet system to check whether this additional temperature is equivalent to the former. New measurements in the [720-900] nm range will likely allow observing atomic O radiation, specially from the

triplet at 777 nm, and the plasma thermal equilibrium condition will be checked using this additional method.

4.2. Chemical equilibrium

The temperature T of the plasma is now know, and a nearly flat temperature profile is obtained in the plasma radiative region, which is the region of interest. This plasma parameter allows us to determine further the equilibrium degree of the plasma, namely, the chemical equilibrium condition.

Initially, we've got to determine the thermal history of the plasma gas when it enters inside the induction coil. Knowing the plasma temperature in the measurement region, the approximation that the plasma gas temperature starts from 300 K and reaches 6000 K is made. A simple calculation based on the application of the Fourier's law leads us to estimate the time required to heat the gas:

$$\Delta t = \frac{\lambda \cdot S \cdot \Delta T}{v \cdot \phi} \qquad (3)$$

where λ is the thermal conductivity of the CO_2 (0.017 W/m K), S the quartz tube section, ΔT the temperature variation, v the plasma gas velocity (0.173 m/s) and ϕ the power transferred to the plasma (40% of the injected power is supposed to be transferred into the plasma, which is underestimated). The order of magnitude of Δt is 0.2 ms which is more than two orders of magnitude lower than the flow residence time.

Secondly, the determination of the reaction rates is realized to show if chemical equilibrium is reached in a time inferior to 30 ms for the considered temperature. This is the matter of the following paragraph.

4.2.1. Reaction rates calculation

It was assumed that the plasma was steadily heated from 300 to 6000 K throughout the induction coils to the measured section. Therefore, the plasma is heated to an amount of approximatively 1500 K between two successive induction coils. A one-dimensional calculation of the plasma species concentrations using a reaction rate set was carried in the restrictive hypothesis of an instantaneous temperature rise of 1500 K. This allowed verifying the time needed for an equilibration of the plasma species concentration to the new temperature $T_0 + 1500$ K, starting from equilibrium species concentrations at T_0. This calculated time has to be considered as a majoring value of the actual equilibration time, the temperature rise not being instantaneous, but rather gradual.

A forward reaction rates set (K_f) proposed by Park (Park 1994) for the Martian atmosphere was used in the calculation. Backward reaction rates (K_b) were calculated through the determination of equilibrium constants K_{eq} and the use of the relationship

$$K_b = \frac{K_f}{K_{eq}} \qquad (4)$$

The equilibrium constants were determined through the calculation of the equilibrium concentrations for the Martian-type gas chemical species at given temperatures T. A numerical program using the Gibbs energy minimisation technique has been used to achieve these equilibrium concentrations.

A calculation was carried for an instantaneous increase of a plasma in equilibrium conditions at $T = 3000$ K to a temperature of 4500 K. The time evolution of the chemical species concentration, normalized to their new equilibrium concentrations at 4500 K, is plotted in Fig. 9
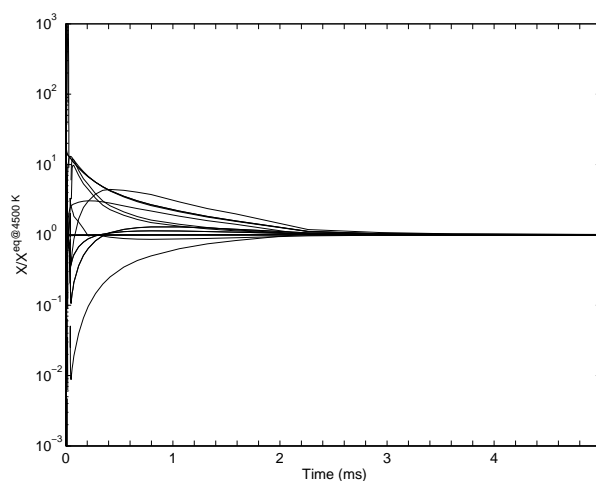
Figure 9. Evolution of the chemical composition of a 97% CO_2–3% N_2 equilibrium plasma at 3000 K instantaneously heated at 4500 K

It is verified that a time interval of no more than 4 ms is needed for achieving chemical equilibrium conditions at this new temperature. This is about one order of magnitude lower than the flow residence time, and chemical equilibrium conditions can be considered to be reached in the region where measurements are carried (moreover, it is reminded that the calculation of the plasma chemical composition evolution is calculated for a restrictive case).

4.2.2. Plasma composition curves

In the ICP torch, the plasma is formed at atmospheric pressure, so all pertinent chemical reactions occur at this pressure. Chemical equilibrium is reached when the Gibbs free energy is at minimum. In order to solve this minimization, two other relations are needed as the electrical neutrality and the Dalton law.

The chemical species taken into account for the calculation are as follows: 11 monatomic species (C, C^-, C^+, C^{++}, N, N^+, N^{++}, O, O^-, O^+, O^{++}), the electrons (e^-), 16 diatomic species (C_2, C_2^-, C_2^+, CN^+, CO, CO^-, CO^+,

N_2, N_2^+, N_2^-, NO, NO^+, NO^-, O_2, O_2^+, O_2^-) and 23 poly-atomic species (C_2N, C_2N_2, C_2O, C_3, C_3O_2, C_4, C_4N_2, C_5, CNN, CNO, CO_2, CO_2^-, N_2O, N_2O_3, N_2O_4, N_2O_5, N_2O^+, N_3, NCN, NO_2, NO_2^-, NO_3, O_3).

Fig. 10 collects the plasma composition calculated for the Martian-like atmosphere at thermal equilibrium. The main species are CO and O for temperatures inferior to 7500 K. For temperatures inferior to 5000 K, the electrical neutrality is made between NO^+ and e^- whereas for temperatures superior to 7000 K, it is made between C^+ and e^-. Fig. 11 represents the mass enthalpy for our plasma as a function of temperature.
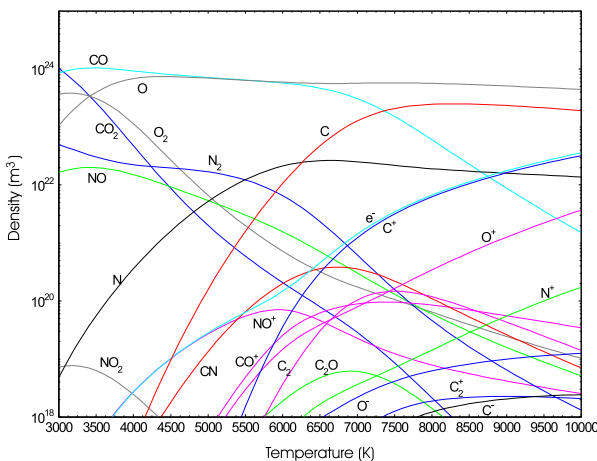

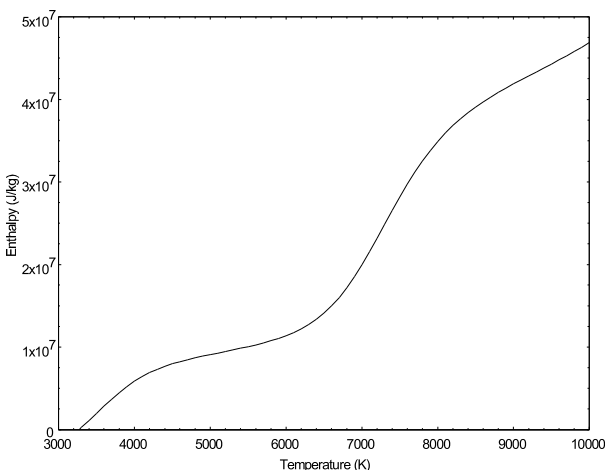*Figure 10. Plasma composition of Mars atmosphere (97% CO_2–3% N_2)*

Figure 11. Massic enthalpy as a function of temperature for a Martian-like atmosphere (97% CO_2–3% N_2)

Such calculations, along with the determination of the radial temperature profiles of the plasma and the verification of the thermodynamic equilibrium of the plasma, allow determining the local species concentrations in the plasma. These overall parameters (temperature and species concentration profiles) suffice in order to allow setting up a simulation of the radiative emission of the plasma along it's radius. Such calculations can then be

compared against the overall measured and calibrated spectra in order to estimate the accuracy of the spectral datasets used in the calculations.

5. CONCLUSIONS

A new testcase for the validation of radiative codes simulating equilibrium radiation from a Martian-type plasma in equilibrium conditions in the near-UV to near-IR range has been defined. First investigations lead to the confirmation that the plasma is in thermodynamic equilibrium conditions in the measurement region. Such investigations have to be confirmed through excitation temperature T_{exc} determination by atomic line radiation measurements in the [720-900] nm region. Moreover, it would be interesting to calculate the radial electron diffusion rates in order to check if a departure from thermodynamic conditions can be favored by this process.

The radial temperature and species concentration profiles can be provided in order to carry a one-dimensional radiative transfer calculation and compare the calculated spectrum to the measured one. The methodology for the calculation is the same than the one described in (Laux 1993).

Finally, as theoretical radiation calculations show that most of the radiation of a Martian-like plasma will be emitted in the vacuum-UV and infrared regions (Lino da Silva 2004), it would be interesting to extend the spectral range of such measurements to these additional regions in order to provide more validation data for spectral codes.

ACKNOWLEDGMENTS

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