
Spectroscopic Measurements in Plasma Flows

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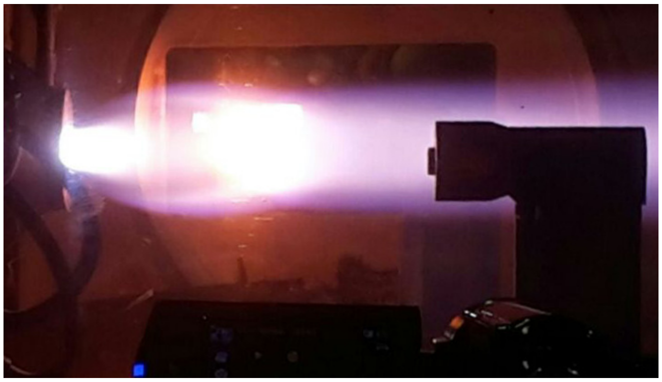

Figure 1: Barrel shock in the VKI plasmatron

1 Introduction

This report addresses the post-processing of some spectroscopic data, in the 200 - 1000 nm range, coming from measurements made in a plasma wind tunnel. Far from being exhaustive, this document is just an informal student report dealing with the basics of spectroscopy.

Plasma wind tunnels (ICP or arcjets) prove to be a unique tool in the study of the atmospheric entry of space vehicles, one very big issue being the design of the thermal protection systems (TPS) or the study of surface catalicity. A lot of information on the state of plasma flows can be retrieved with spectroscopic measurements, such as the temperature and concentration of chemical species. Such information can be used to develop numerical prediction tools and models.

The experimental method chosen is the **emission spectroscopy**. First of all the calibration of the spectrometer is checked in terms of wavelength by analyzing the emission of an Hg lamp. The raw signal coming from a plasma stream is then analyzed to identify the major species. Finally, a graphite sample is inserted in the plasma jet and a spectral fitting is performed in order to estimate the translational and electronic temperatures of the plasma. A nice picture of a supersonic jet is shown in fig. 1. The jet is seen to be underexpanded and the barrel shock structure is clearly visible.

Alert: data and methods here reported may be misleading or even wrong and are just intended to give an overview of the techniques in this field.

2 Calibration

As for virtually all experimental measurement techniques, the very first step consists in calibrating the acquisition chain. The working principle of CCD-based spectrometers is splitting the radiation into its components at different wavelengths, and direct each of them to a different pixel. The splitting of the light beam is usually achieved using a *diffraction grid*.

The calibration process is twofold:

- first of all each pixel needs to be mapped to the incoming wavelength and this can be done by observing radiation lines coming from a known source
- secondly, the measured amplitude from pixels needs to be linked to the real intensity of the light.

Only the former procedure is here analyzed. A mercury lamp was observed and the spectra was compared to emission lines of Hg, retrieved from the NIST database [1].

In fig. 2 the spectrum and the Hg lines from NIST are compared, showing a mismatch of around 0.5 nm, that is below the 1 nm resolution of the instrument. Table 1 shows some Hg transitions, from the NIST database, and their associated Einstein coefficient. Should be recalled that the emission intensity for a given transition is related to both the Einstein coefficient A_{ij} of the transition and the level population N_i:

$$\epsilon_{ij} = N_i \frac{A_{ij}}{4\pi} \frac{hc}{\lambda_{ij}} \tag{1}$$

where h is the Planck's constant, c the speed of light and λ_{ij} the transition wavelength.

wavelength λ [nm]	**Einstein coeff.** A_{ij} [s^{-1}]
237.8324	3.6e+06
253.6521	8.4e+06
265.2039	3.9e+07
296.7283	4.6e+07
302.1504	5.1e+07
312.5674	6.6e+07
365.0158	1.3e+08
365.4842	1.8e+07
404.6565	2.1e+07
407.7837	4.0e+06
435.8335	5.6e+07
546.0750	4.9e+07
576.9610	2.4e+07
690.7460	1.6e+06

Table 1: Atomic emission lines for Hg, from NIST database.

The calibration procedure for the intensity is not reported in this document, however it constitutes a necessary step if the plasma temperature is to be retrieved. Basically, the procedure reduces to observing a source with a known temperature and emissivity. Usually, a tungsten lamp is used: since the source is a solid, the emitted radiation closely follows a Planck curve and the calibration reduces to finding the corrective function that matches the observed spectrum amplitude to the theoretical curve.

3 Free-stream analysis

This section deals with the analysis of the plasma jet free stream from a spectroscopic point of view. First of all atomic species will be identified from the measured spectrum, using the NIST database. The plasma temperature is then determined using the intensity of two atomic lines. Finally, attention will switch to molecular species, identified using both literature and the Specair software.

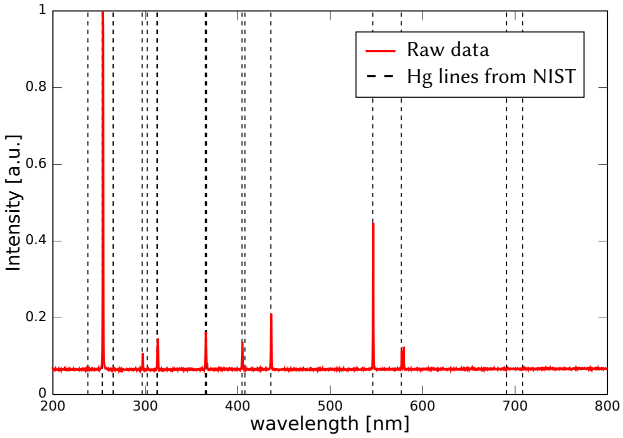

Figure 2: Raw Hg spectra superimposed to observed lines

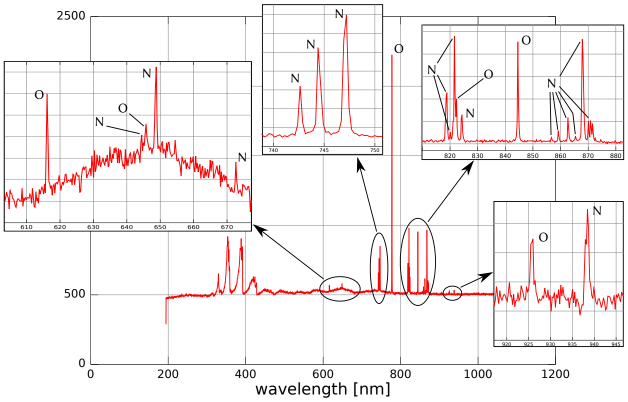

Figure 3: Atomic species identified in the free stream.

3.1 Atomic species

Radiation emitted by atoms has a sharp footprint. Photons emitted by **atoms** result from transitions of bound electrons from one orbital to a lower energy one. Such a jump results in a release of energy of a given and isolated wavelength and thus results in sharp peaks on the spectrogram. On the other hand, as will be explained later, **molecules** produce much broader signatures in the spectrum, see [2]. The spectrum is reported in fig. 3, together with some identified emission lines. The well known oxigen line at 777 nm is very visible, as well as the 822 nm line. Those two lines will be used in the next paragraph to determine the plasma temperature.

The emission intensity is known to be dependent on the population of the excited levels N_i and on the Einstein coefficients of the transition A_{ij}, as given in eq. 1. In the hypothesis of thermal equilibrium, the population N_i follows a Boltzmann distribution:

$$N_i(T) = N \frac{a_i}{Q(T)} \exp\left(-\frac{E_i}{k_B T}\right) \tag{2}$$

N being the number density of particles (particles per cubic meter), $Q(T)$ the partition function, a_i the degeneracy of the energy level, E_i the level energy and k_B the Boltzmann's

constant.
Notice that the population N_i is a function of the temperature, and this implies that:

- different temperatures give rise to different lines intensities
- from the lines intensities it's possible to determine the species temperature.

As said, lines were identified using the NIST database [1]. Along with the emission wavelengths, the database provides much useful information about the radiative transitions, such as the degeneracies of electronic levels, the Einstein coefficients A_{ij} (transition probabilities) and "intensity index" giving a rough idea of the emission intensity at standard conditions.

Despite atomic emission is theorized to show up as a line, what is observed is a **broadened** peak. This is partially due to the spectral resolution of the spectrometer and partially due to well known physical mechanisms: Doppler broadening, collisional broadening and (in some particular cases) Stark broadening (effect due to the perturbation of the energy levels due to Coulomb potential).

3.2 Temperature determination

In the hypothesis of thermal equilibrium (Boltzmann distribution), the temperature of the plasma can be retrieved by analyzing the oxigen 777 and 822 nm peaks intensity. The intensity has to be calibrated and Abel-inverted (process not shown here).

The process for retrieving the temperature proceeds as follows: first of all the population N_i of the two oxigen lines is found using the emission intensity, eq. 1. The Boltzmann distribution is then used for the two points to find the translational temperature. Temperature is found to be around 7820 K.

By plotting the populations as done in figure 4, it's possible to include emission data from more spectrum lines, and obtain the temperature as the slope of the linear fitting. Finally, plotting more than two emission lines shows if the population is actually following a Boltzmann distribution (points are on a straight line) or if the flow is out of equilibrium.

3.3 Molecular species

Molecular species produce a spectrum which is much more complex than atomic spectra. In fact, in addition to electronic energy levels, molecules can also store energy in the form of vibration or rotation. Transitions among purely rotational or purely vibrational levels usually result in emission of radiation in the range of the microwaves and far infrareds respectively and cannot be observed with the employed experimental setup. On the other hand, transitions involving a change in both electronic and vibrational/rotational level appear in the observed spectrum.

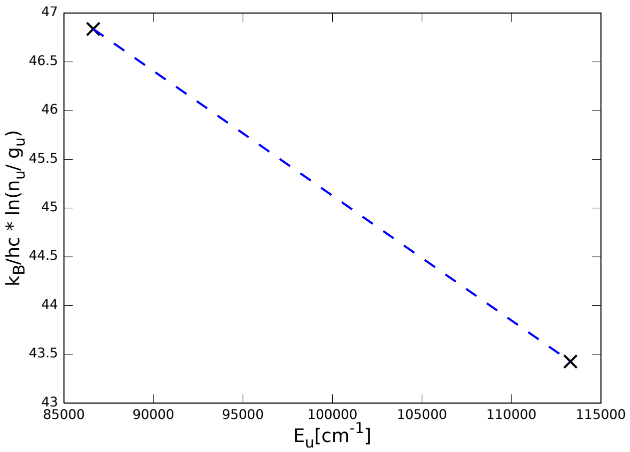

Figure 4: Levels population and temperature fitting.

Since rotational and vibrational energy levels are *much* more closely spaced than electronic levels, mixed transitions generate a series of very closely spaced lines on the spectrum, so close that are resolved as one only broad signature by the spectrometer.

The footprints of molecular transitions were retrieved from literature [3], and using SPECAIR the detailed structure was plotted. By analizing the wavelength of the peaks it was then possible to recognize the species in the plasma, as shown in figures 5 and 6. An overview of the observed molecular emission is given in figure 7. The molecular spectra is seen to be generated mainly by N_2^+, CN and N_2.

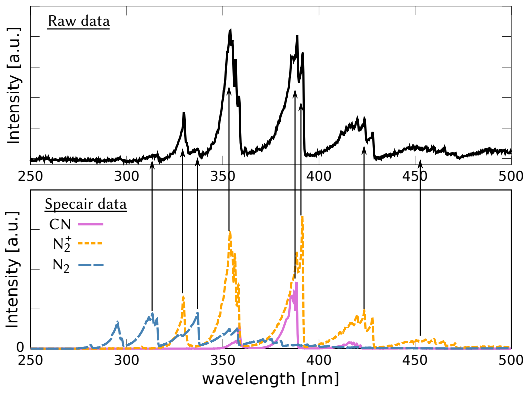

Figure 5: Molecular spectra in the band 250-500 nm

Each molecule shows various structures in the band 200-500 nm: those are due to the same jump in electronic energy, but different changes in the vibrational state (see [3]). As anticipated, the structures are quite spread and this is to be attributed to jumps to different rotational levels.

Recalling that the observed jet is composed of atmospheric air, the presence of carbon can be assumed to be extremely low with respect to oxigen and nitrogen species. Nonetheless, a significant portion of radiation is seen to be

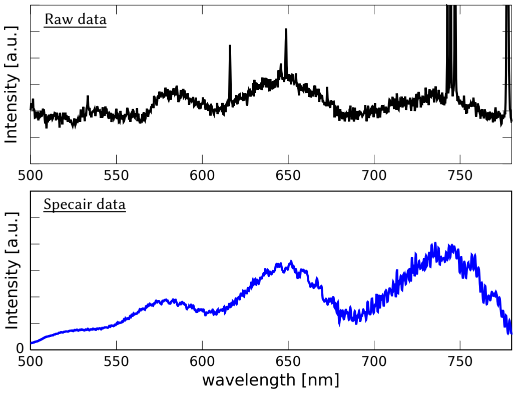

Figure 6: Molecular spectra in the band 500-790 nm: N_2^+

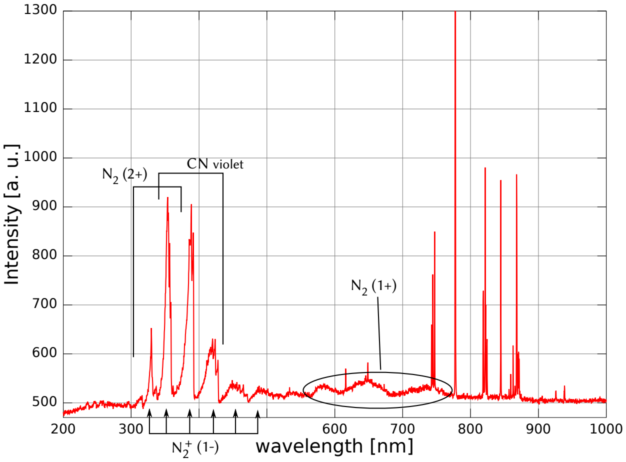

Figure 7: Emission due to molecular transitions

due to CN-violet system, that notoriously generates very strong emission.

The reader may be puzzled by the fact that Specair gives spectra which are quite different in terms of amplitude than the observed ones: in fact, in the present section the software is used in a purely qualitative way. A more accurate spectral fitting will be performed in the next section, leading to good reproduction of the experimental spectra (fig. 10).

4 Graphite ablation

After acquiring data on the freestream, a graphite sample is introduced in the jet and the spectrometer is pointed to the boundary layer, to analyze the flow in the vicinity of the stagnation point.

Two activities are here reported:

- the wall temperature is assessed by fitting the Planck's law to the experimental spectrum
- the plasma temperature is retrieved by fitting the spectrum.

4.1 Wall temperature

The spectrum in the boundary layer is the superposition of the emission from the plasma and from the wall. As well known, the spectrum emitted by a solid (the wall) follows the Planck's curve - at least, in the ideal black body case. The Planck's law can thus be exploited to retrieve the wall temperature.

Figure 8 shows the Planck curves (eq. 3) for various surface temperatures.

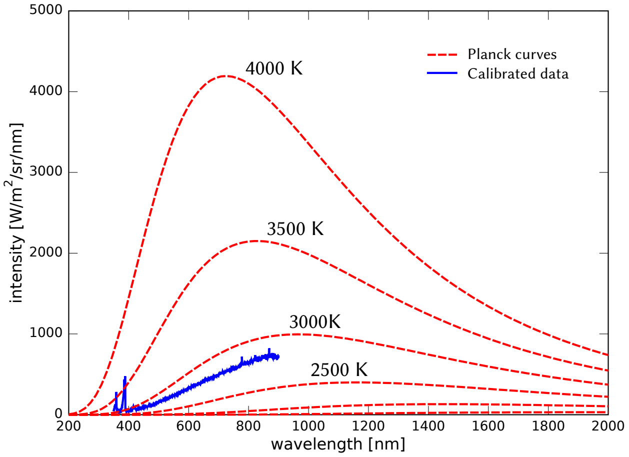

Figure 8: Planck's curves for various temperatures

$$I(\lambda,T) = \frac{2hc}{\lambda^5}\frac{1}{e^{\frac{hc}{k_B T\lambda}}-1} \tag{3}$$

Attention should be paid to the fact that the Planck's law here used is function of the wavelength. Switching from the frequency to the wavelength is not simply a matter of changing variables, but should be done by:

$$I(\lambda,T)\ \mathrm{d}\lambda = -I(\nu,T)\ \mathrm{d}\nu \tag{4}$$

A fitting was performed manually, revealing a wall temperature T_w of around 2820 K. The result is shown in figure 9. Mind that in case of *grey body*, the surface emissivity should also be taken into accout.

4.2 Plasma temperature - CN fitting

Near the surface of the graphite sample, the amount of carbon in the plasma is dramatically increased, leading to an increase in the CN-violet emission. CN is the leading emitting molecule in this region and its spectrum can thus be used to perform a temperature fitting. A thermal nonequilibrium fitting was performed using Specair, returning a translational temperature of 7900 K and a much higher internal one. The initial and final optimization steps are shown in figure 10.

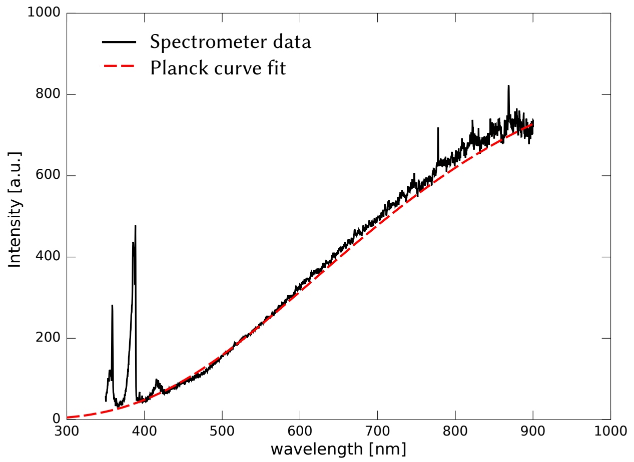

Figure 9: Fit of the spectrogram using the Planck's law

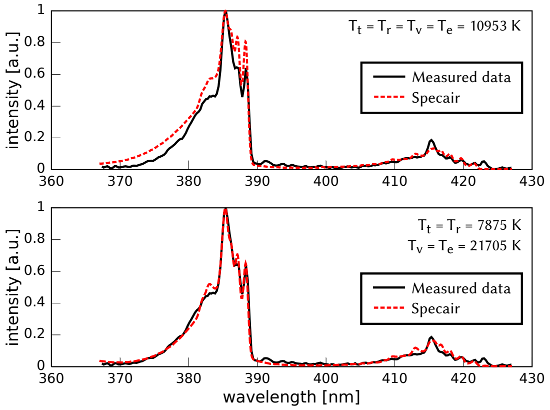

Figure 10: Optimitation process for spectrum fit. Top: first optimization step (LTE). Bottom: final fit - two temperatures.

5 Conclusions

This work reviewes some experimental techniques useful in analyzing plasmas using emission spectroscopy:

- first, the calibration procedure is briefly reviewed
- then, a jet is analyzed in terms of temperature and chemical species
- finally, a graphite sample is inserted in the flow and the wall and plasma temperatures are retrieved.

I hope you enjoyed.

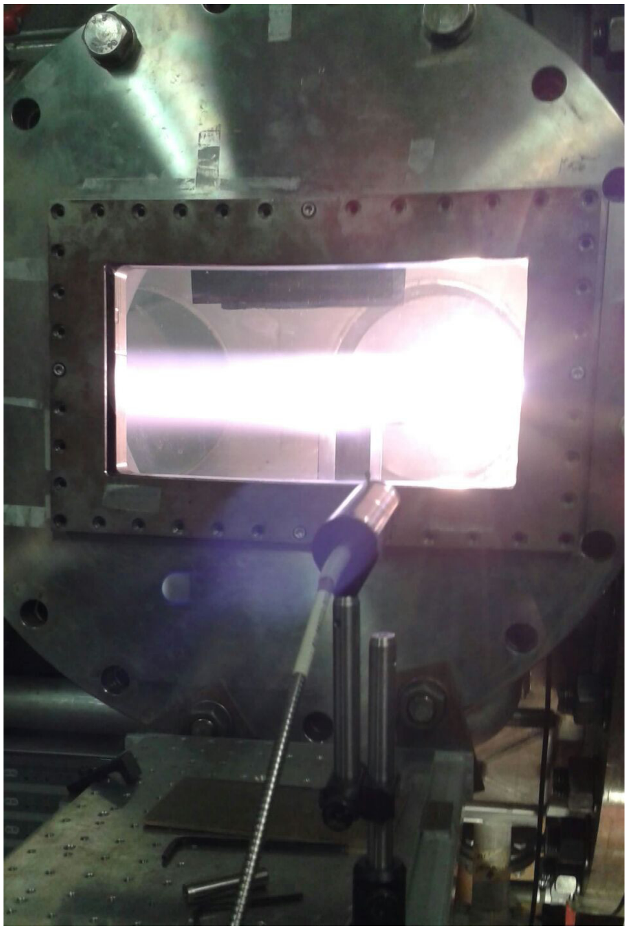

Figure 11: Ablation test on a graphite sample.

References

[1] NIST atomic lines database, `http://physics.nist.gov/PhysRefData/ASD/lines\_form.html`

[2] D. C. Harris and M. D. Bertolucci, *Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy*, Dover Publications, 1979.

[3] D. Le Quang Huy, *Spectroscopic measurements of Sub- and Supersonic plasma flows for the investigation of atmospheric re-entry shock layer radiation*, PhD thesis, Université Blaise Pascal, 2014.