

Contents

1	Spectral Analysis	3
1.1	Radiation emission	3
1.2	Experimental setup	4
1.3	Line recognition	5
1.4	Relative intensities	9
1.4.1	Pulse settings	9
1.4.2	Line of sight	9
1.5	Estimation of plasma temperatures	10
1.5.1	Rotational temperature for OH and for N ₂	11
1.5.2	Vibrational temperature for N ₂	11

Chapter 1

Spectral Analysis

A fundamental aspect of the Plasma Coagulation Controller is what species are produced and deposited during its application. Various studies observed the spectrum of plasma DBD discharge in air at atmospheric pressure and ambient temperature ([4], [5]), mainly it presents peaks relative to reactive species from water, oxygen, nitrogen and its oxides at visible wavelength, from 200 to 880 nm.

We are interested in plasma that contains molecules involved in blood coagulation mechanisms, Reactive Oxidant Species (such as hydroxyl radical OH) and Reactive Nitrogen Species (derived from nitric oxide NO) ([13]). In this spectroscopy study is given particular attention to them and their precursor, i.e. the presence of transitions relative to hydroxyl, oxygen and molecular nitrogen.

1.1 Radiation emission

As remembered in previous chapters, at the exit of source head is produced plasma from a mixture gas of helium (or argon) and air, so along free electrons, there are ions and species that colliding with them are in an excited state, metastable or with small lifetime. All those reactive species participate in different reactions, and also in excitation and de-excitation reactions with consequent emission of radiation. When an electron goes from state p at higher energy to state k of lower energy, is emitted radiation with central wavelength λ_0 . Power emitted by this radiation is given by radiant flux $d\phi_\lambda$ and selecting a solid angle as in figure, is possible to define radiance L_λ , and intensity I , as in equations 1.1. Intensity for a radiation ultimately depends on $n(p)$, population density for state p , and Einstein Coefficient for the transition A_{pk} that is typical for the transition ([1]).

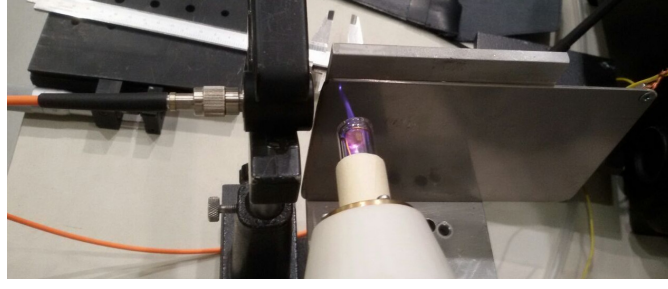
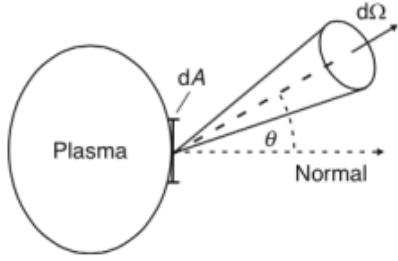


Figure 1.1: Setup of the experiment: there is the working source, the metal target and the optical setup on the left.



$$\begin{aligned}
 \lambda_0 &= \frac{hc}{E_p - E_k} \\
 L_\lambda &= \frac{d^2\phi_\lambda}{dA \cos(\theta) d\Omega} \\
 I &= \int L_\lambda d\lambda = n(p) A_{pk}
 \end{aligned}
 \tag{1.1}$$

Using air as gas, composed by molecules, at visible wavelength are observed vibronic transitions where molecule goes from a vibrational state to another, with a change of vibrational quantum number ν , and/or from a rotational state to another, with change of quantum number J ([7], [17]). When there is a vibrational transition, each line corresponds to different numbers $\nu' - \nu''$, these are transitions well spaced in the spectrum, easy to recognize. Rotational transitions gives birth to bands of little-spaced peaks hard to resolve whitout an efficient spectrometer.

There are many reactions involving oxygen and nitrogen (see for example [11]), in this study we determine only principal transition observable with our spectrometer, to know dominant reactive species present in our plasma plume.

1.2 Experimental setup

For the source it's used a prototype that presents electrical specifics and settings same as source A described in previous chapters. A metal plate is positioned as target at a distance of 10 mm from plasma exit. To ignite plasma is used helium, with flow set to 2L/min. To measure emission it's used a spectrometer IsoPlane, that thanks to diffraction separates emissions with different wavelengths using a plane grating. The spectrometer has a focal lenght of 320 mm and is equipped with three different gratings: 150, 1200 and 2400 gg/mm, corresponding to different resolutions. As in figure 1.1, light emitted by plasma is collected with a quartz lens and passes trough an optical fiber connected to the spectrometer entry, while at the spectrometer exit there is a CCD camera of 2048 pixels and a count limit of 65 000.

Once a grating is chosen, the acquisition system can be set at a starting wavelength and from there it takes measures until the end of the CCD, so for a different wavelength interval for different gratings. For every measure is selected an appropriate acquisition time that permits to observe peaks with a good count number and avoid saturation.

It's important to stress out that, with this measuring method and due to complexity of plasma reactions and composition, it's not possible to extrapolate quantitative considerations between different species concentration. However it's possible to recognize the presence of certain species and make some considerations watching spectra variation with different experimental setup.

An interesting parameter is the working distance between source's head and target, so we observe spectra focalizing the lens in two different positions:

- position 1: as close as possible to plasma exit point
- position 2: close to the target, at 10 mm from plasma exit point

Reactions that produce and recombine reactive species, and consequently density and lifetime of species, are influenced by electric field and duration of the discharge. We observe spectra changing amplitude and frequency of the pulse, with three different combinations that corresponds to different power coupled with the discharge:

- low: $f = 5 \text{ kHz}$ and $\Delta t = 15 \mu\text{s}$
- medium: $f = 10 \text{ kHz}$ and $\Delta t = 10 \mu\text{s}$
- high : $f = 15 \text{ kHz}$ and $\Delta t = 10 \mu\text{s}$

1.3 Line recognition

To see what's generally produced in a discharge is taken a spectrum for the entire wavelength's region intersted, from 230 to 800 nm, with standard setup of medium power and position 1. First is made a rapid acquisition with the lowest resolution possible, to see interesting regions and have an idea of required exposition times. After that is made a slow acquisition with higher resolution for all wavelengths. The entire spectrum is reconstructed attaching different spectra, showed in figure 1.2, where are labelled principal transitions. For every measure is taken also a background spectrum, without plasma, to recognize peaks that are not from the plasma.

Data is read with IDL routines ([6]) and analyzed with ROOT TSpectrum.h library ([14]). Every spectrum is divided by its exposition time, to normalize different measures. Then is estimated the white noise contribution as mean value from a portion of the spectrum that doesn't presents peaks and its subtracted to the counts for each wavelength. Peaks are then found with TSpectrum functions (where is possible to set a treshold in height and the general width for lines to be searched) and peaks from background are isolated in plasma spectra. Definitive position for each transition is found with a gaussian fit in an interval that takes into consideration the asymmetry where it's needed.

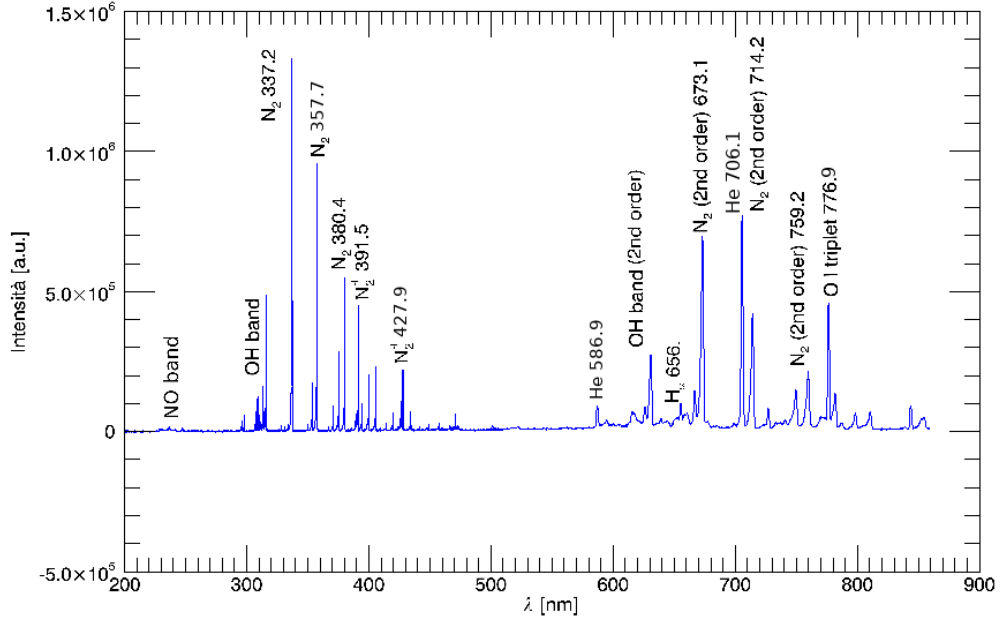


Figure 1.2: Spectrum with an helium flow of 2 L/min, pulse parameters of $f = 5$ kHz and $\Delta t = 16$ μ s, optical position 1, near plasma exit

As said before, this study is focused on measure related to ROS and NRS, so in lines for NO, OH and N_2 .

NO lines Are observed two doublets for the transition $A^2\Sigma^+ \rightarrow X^2\Pi$ with vibrational numbers (0-0) ([10], [16]), presented in table 1.1. Intensities for the peaks are normalized with maximum value of 1000 for the acquisition, the table shows as the intensities for this transition is very low. Other transition relative to this molecule have even lower relative intensity and are not observed in our study.

λ [nm]	I [arb.u.]
236.31 ± 0.24	27
237.00 ± 0.15	26
247.02 ± 0.05	28
247.86 ± 0.12	27

Table 1.1: Peaks measured for NO.

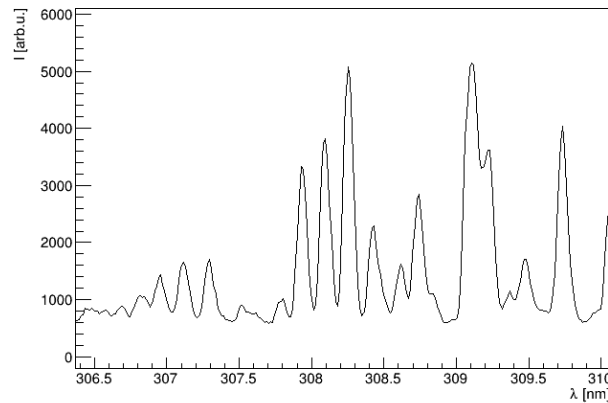
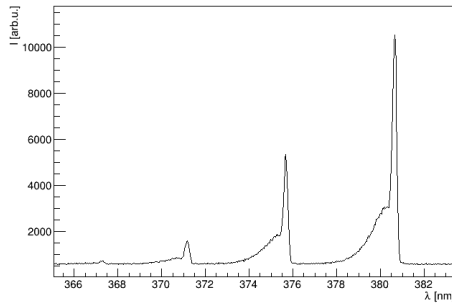
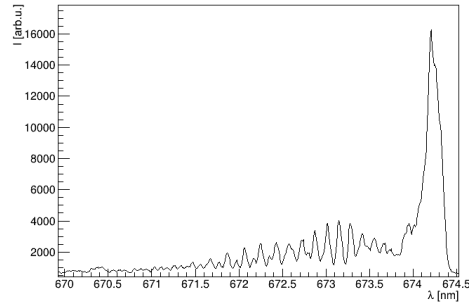


Figure 1.3: Zoom for OH peaks

(a) Transitions with $\Delta\nu = 2$ (b) Strongest line (0-0), 2nd diffraction orderFigure 1.4: Zoom for N₂ transitions.

OH lines Is found the rotational band for transition ($A^2\Sigma, \nu' = 0 \rightarrow X^2\Pi, \nu'' = 0$), observing 13 principal lines ([8]). In figure 1.3 a zoom on the spectrum, in table 1.2 peak values.

N₂ and N₂⁺ lines Measured spectrum presents several lines, including the strongest, for diatomic molecule dinitrogen. Is observed the Second Positive System for N₂ transition $C^3\Pi \rightarrow B^3\Pi$ and the First Negative System for N₂⁺ transition $B^2\Sigma \rightarrow X^2\Sigma$, in table 1.3 peak values ([2], [3]). For N₂ is found also a band of multiple rotational lines centered around 336.58 ± 0.01 nm. Some of the peaks are seen in the second diffraction order, where there is more distance between lines. In figure 1.4 are presented two zooms for N₂ lines.

Atomic lines Are observed other lines from elements present in the plume ([12]):

- **H_α** line corresponding to transition from quantum number $n = 3$ to $n = 2$

λ [nm]	I [arb.u.]
306.96 ± 0.01	53
307.11 ± 0.01	58
307.29 ± 0.01	62
307.94 ± 0.01	142
308.09 ± 0.01	148
308.26 ± 0.01	161
308.43 ± 0.01	112
308.62 ± 0.01	46
308.74 ± 0.01	137
309.11 ± 0.01	151
309.22 ± 0.01	120
309.45 ± 0.01	36
309.73 ± 0.01	125

Table 1.2: Peaks measured for OH.

	λ [nm]	I [arb.u.]	$(\nu' - \nu'')$
N_2	316.03 ± 0.01	381	(1-0)
	337.11 ± 0.01	1000	(0-0)
	357.77 ± 0.01	722	(0-1)
N_2	367.22 ± 0.20	58	(3-5)
	371.12 ± 0.04	172	(2-4)
	375.66 ± 0.02	232	(1-3)
	380.64 ± 0.02	423	(0-2)
N_2^+	391.50 ± 0.02	355	(0-0)
	427.45 ± 0.02	180	(0-1)

Table 1.3: Peaks measured for N_2 and N_2^+ .

	λ [nm]	I [arb.u.]
H $_{\alpha}$	655.96 ± 0.04	113
He	586.94 ± 0.05	122
	705.56 ± 0.01	649
O	776.89 ± 0.01	393

Table 1.4: Main peaks measured for other species found in plasma.

- **He** two of the strongest lines for helium
- **O** strong line of oxygen

1.4 Relative intensities

From comparison of spectra with different discharge parameters and different position for light collection point, is possible to extrapolate some informations on production rates of excited species.

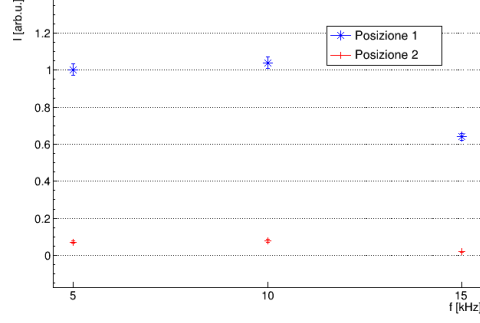
Intensities are evaluated for OH and N₂ species, collectively for the lines in a wavelength range specific for the peaks. For OH lines is considered all the rotational band between 306-309 nm, lines for N₂ are separated in those between 335-337 nm (rotational band and (0-0) transition) and those between 368-382 nm (vibrational transitions with $\Delta\nu = 2$).

1.4.1 Pulse settings

Pulse settings characterize the discharge. As seen in chapter ?? for different frequencies we have near the same electric behavior, but it could influence specie's production rates. OH lines for both positions have same intensity with low and medium power setup, while is lower with higher frequency, with similar behavior in both positions. N₂ intensities also decrease with higher frequencies, for every lines, it reaches around 0.6% for $f = 15$ kHz in position 1, and lower values for position 2. It seems that production of those reactive species have rates dependant from pulse frequency, for high frequency there might be more relevant competitor reactions.

1.4.2 Line of sight

Positioning the line of sight of the spectrometer at different heights along the plume axis, we can extrapolate informations about the lifetime of the species and the distance that they can travel. At 10 mm from the source, in position 2, intensities for OH decreases drastically, under 0.1% of values in position 1. OH species seems to have small lifetime or mobility, so deposition of this species is higher when closer to the target. For N₂



(a) OH intensities in range 306-309 nm

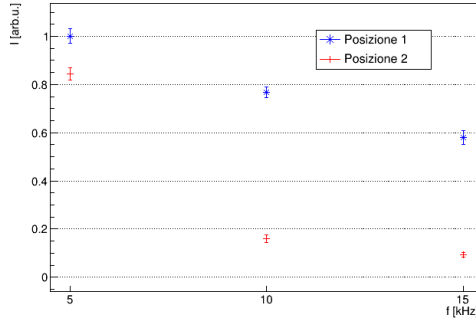
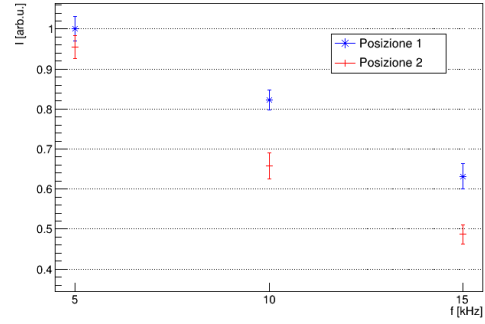
(b) N₂ intensities range 335-337 nm(c) N₂ intensities range 368-382 nm

Figure 1.5: Relative intensities in selected portions of the spectrum, for different frequencies, in blue for position 1 in red for position 2.

intensities are equal at low frequency for both positions, while for higher frequencies they decrease more for position 2. For low frequency, concentration of excited N₂ is high so even distant from the target we have high radiation emission. When it decreases, for higher frequencies, concentration lowers and we have few molecules that reach the target.

1.5 Estimation of plasma temperatures

From diatomic molecule's spectra it's possible to evaluate some parameters that are indicators of plasma's state: rotational temperatures for OH and N₂, T_r , and vibrational temperature for N₂, T_v . These parameters are estimation of the temperature at which thermal energy is comparable to the gap energy between rotational or vibrational state transitions, they can be defined as in equations 1.2 where ν is the vibrational quantum

number and I is the quantized moment of inertia of the molecule.

$$\begin{aligned} T_r &= \frac{\hbar^2}{2k_B I} \\ T_v &= \frac{h\nu}{k_B} \end{aligned} \tag{1.2}$$

Rotational temperatures can be considered an estimation of neutral gas kinetic temperature, assuming that the population origins only from heavy particle collisions. Vibrational temperature gives an idea of the population of vibrational states, useful to determine chemical reactions inside plasma.

1.5.1 Rotational temperature for OH and for N₂

In rotational bands the intensity of a transition for a specific wavelength is proportional to the number density population of upper state (equation 1.1), that, considering a Maxwell-Boltzmann distribution, is proportional to the temperature of the species. In equation 1.3 the proportionality is explicitated, with D_0 parameter that depends on number of initial molecules, partition function of the rotational state and quantum rotational numbers for upper and lower state, S is the oscillator strenght specific for the molecule and E_r depends from a constant defined by the vibrational state and from quantum rotational number for upper state ([15]).

$$I = \left(\frac{2\pi}{\lambda}\right)^4 D_0 S \exp\left(-\frac{E_r}{k_B T_r}\right) \tag{1.3}$$

Given the high number of rotational lines, not distinguishable with our spectrometer, an approach to temperature estimation is to simulate spectra with different temperatures and to minimize differences for measured spectrum ([9]). In a predetermined range of temperatures we simulate different spectra with different temperatures, where each line is a gaussian peak with its width that takes into consideration broadning due to thermal motion, Doppler effect and measure resolution. For every spectrum is calculated the mean square difference, the temperature si selected as that associated with the minimum difference and are taken upper and lower limits where difference is larger by 5% of the minimum value. An example of the spectra is in figure 1.6, while resulting temperatures are in figure 1.7.

From estimated temperatures we can see that they are compatible with each other, for every distance and for every pulse setup. It's then possible to evaluate a mean value for the species, that are $T_{r,OH} = 352 \pm 38$ K and $T_{r,N_2} = 321 \pm 41$ K, compatible with each other, and that, as said before, can be taken as an indicator of kinetic temperature for neutral species, so as temperature of the gas. This temperatures are a little higher then expected, but it can still be defined a cold plasma.

1.5.2 Vibrational temperature for N₂

Given a set of vibrational transition lines with defined $\Delta\nu = \nu' - \nu''$, their relative intensities are correlated to each other, with a proportionality that involves vibrational

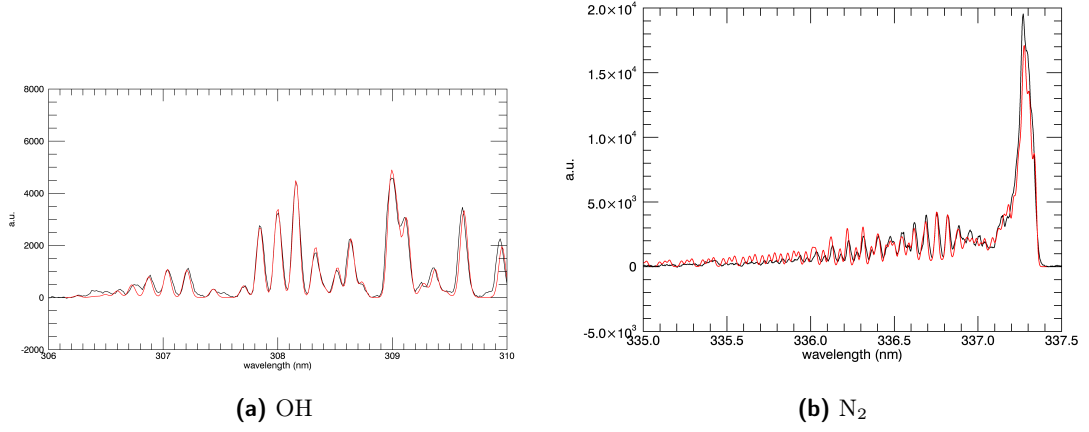


Figure 1.6: Example of optimal spectrum simulation for considered species.

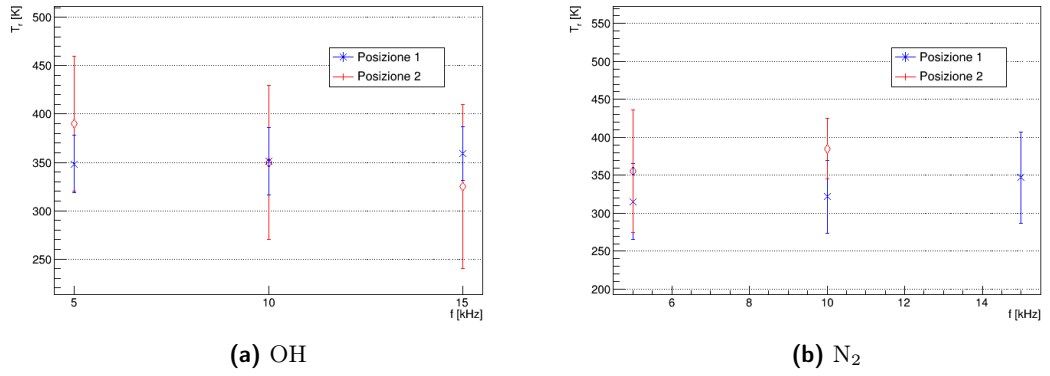


Figure 1.7: Estimation of rotational temperature of OH and N₂ molecules, for different frequencies, in blue position 1 in red position 2.

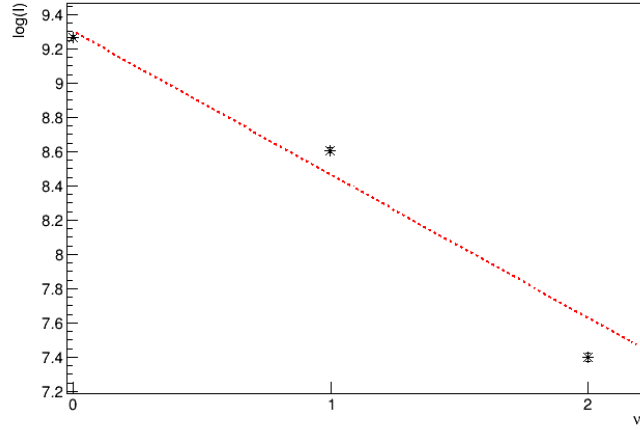


Figure 1.8: Example of a boltzmann graph for estimation of vibrational temperature, for low pulse setup and position 1.

temperature ([3]). Once estimated peak's intensities for considered transitions, it can be made the Boltzmann graph as in figure 1.8 and from then calculate T_v as in formula 1.4.

$$\begin{aligned} \log(I(\nu')) &= S\nu'' + I_0 \\ T_v[K] &= \frac{10^4}{3.57 \cdot S - 0.03} \end{aligned} \tag{1.4}$$

Results are presented in figure 1.9. For this parameter we have values compatible with each other at low and medium power pulse settings with a mean value of $T_v = 3405 \pm 154$ K, while we find a lower temperature for high power pulse settings $T_v = 2781 \pm 322$ K. It seems that with an higher pulse frequency we have lower concentration of excited N_2 produced with lower mean energy.

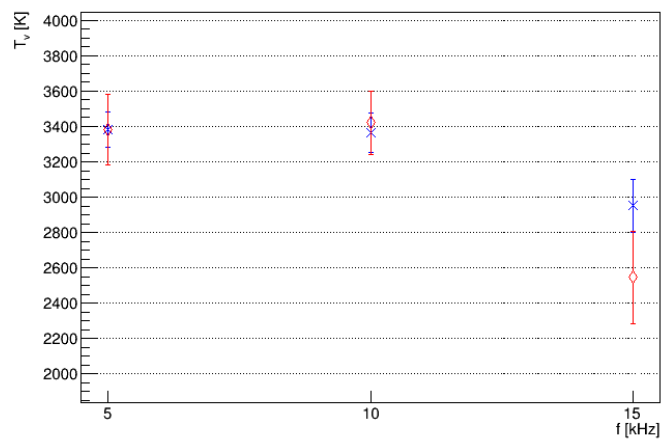


Figure 1.9: Estimation of vibrational temperature of N_2 molecule, for different frequencies, in blue position 1 in red position 2.

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