Emission spectroscopy: Gas temperature

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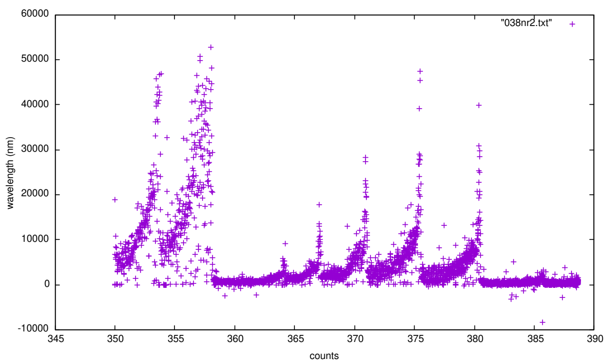
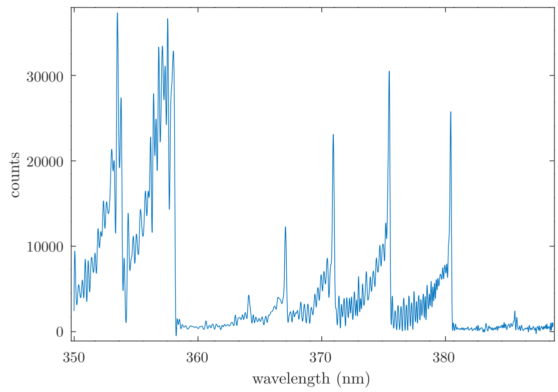
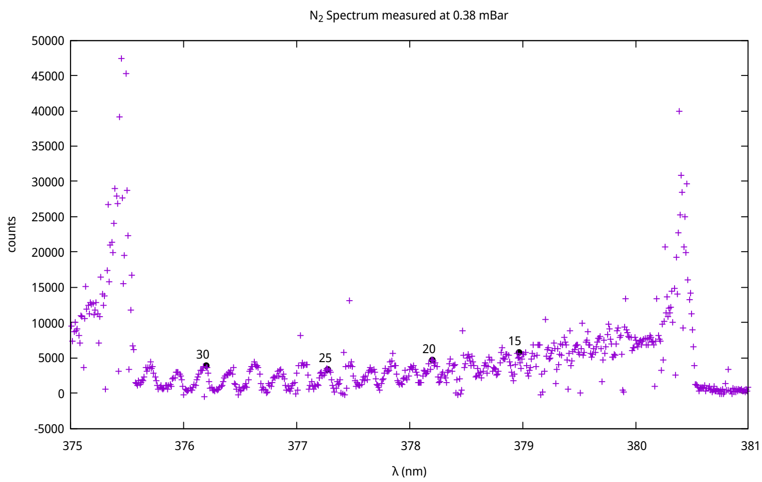
1 Typical Discharge Spectrum





In the figure above the recorded spectrum of a N_2 containing plasma is shown, left is the raw data and right is the splined version.The observed peaks are due to vibrational transitions, inbetween those peaks there are rotational transitions:



In the above figure the numbers on the peaks are the rotational J quantum numbers. Rovibrational transition energies arise due to interatomic distance changes and rotational resonances. How these arise can be qualitatively derived as follows: To derive the vibrational energies, let r_{eq} be the equilibrium distance of the 2 N atoms and add a small displacement of the size $x = r - r_{eq}$. This will give (first order) a force of F=-kx yielding a potential energy $V(x) = \frac{1}{2}kx^2$. Plugging this into the Schrödinger equation:

$$-\frac{\hbar}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi(x) + \frac{1}{2}kx^2\psi(x) = E\psi(x) \tag{1}$$

We get the harmonic oscillator with quantized energy levels

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega \tag{2}$$

I.e this is where the $v' - v'' = 2$ - 0 band notation comes from, we're looking at a particular vibrational band. Each vibrational level comprises a fine structure of rotational energy levels which can also be qualitatively derived: classically the kinetic energy of rotation is

$$T = \frac{1}{2}I\omega^2 = \frac{(I\omega)^2}{2I} = \frac{\mathbf{L}^2}{2I} \tag{3}$$

Since there is no potential energy, the Hamiltonian of the system is just $H = \frac{\mathbf{L}^2}{2I}$, so the Schrödinger equation is:

$$\frac{\mathbf{L}^2}{2I}\psi(\theta,\phi) = E\psi(\theta,\phi) \tag{4}$$

Since the eigenfunctions of the squared angular momentum operator are the spherical harmonics $Y_{lm}(\theta,\psi)$ with eigenvalues $l(l+1)\hbar^2$, we see that the rotational energy levels of our simplified molecule system are

$$E_l = \frac{\hbar}{2I}l(l+1) \tag{5}$$

And thus, if you interchange l with J you see where the rotational spectrum numbers come from. In general however, this is more complicated and can't be calculated analytically (this was only a qualitative explanation), it should be calculated using post-HF methods or DFT.

1.1 notation

Aside from the $v' - v''$ and J, there's more notation needed, the molecular notation of diatomic molecules works as follows:

- The ground electronic state is labeled x with excited states denoted A,B,C,...
- The sum of the projections of the orbital angular momenta on the line connecting the two atoms is labeled Λ, based on this the electronic states are labeled Σ ($\Lambda = 0$), Π ($\Lambda = 1$),...
- As is the case with atoms, the multiplicity is given by 2S + 1 where S is the total molecular spin
- lastly the symmetry is indicated by + or -, indicating wheter the electronic wave function changes sign or not by reflection along a plane passing the internuclear axis. (gerade and ungerade is also used)

The electronic state of a molecule is thus labeled $^{2S+1}\Lambda$, the molecular vibrational-rotational transitions are governed by the selection rules

$$\Delta J = J'' - J' = 0, \pm 1 \tag{6}$$

In this the $\Delta J = 0$ transitions are labeled the Q-branch, the $\Delta J = 1$ the P-branch and $\Delta J = -1$ the R-branch

2 Why is the cathode constructed that way?

The cathode is made into a cylindrical shape with a glass screen around it. The choice for the cylindrical shape is as this gives a uniform charge collection and thus a uniform discharge of gas. We wish to analyse wavelengths 375-380.5 nm, taking a look at the paper "The Spectrum Of Molecular Nitrogen" [1] we see that this corresponds to "the first negative spectrum" which is explained on page 148 as: "this system is observed in the negative column of a discharge through nitrogen,...". I.e we want to observe near the cathode, that's why there's a glass screen there.

3 Recorded I/U characteristics:

Table 1: Measured power supply voltage for different plasma currents and different pressures

0.39 mB	I (mA)	Supply (V)	0.9 mB	I (mA)	Supply (V)	1.3 mB	I (mA)	Supply (V)
	4	671		4	850		4	964
	6	766		6	920		6	1013
	8	863		8	1000		8	1073
	10	960		10	1084		10	1138
	12	1059		12	1173		12	1214
	14	1159		14	1265		14	1299
	16	1259		16	1359		16	1389
	18	1359		18	1454		18	1482
	20	1459		20	1551		20	1578

We did measurements at 3 different pressures (see table 1), For each of these we can deduce the plasma voltage by lowering the supply voltage with $V_{\text{drop}} = I[A] * R_{\text{ballast}}[\Omega]$ whereby the ballast is 50 kΩ:

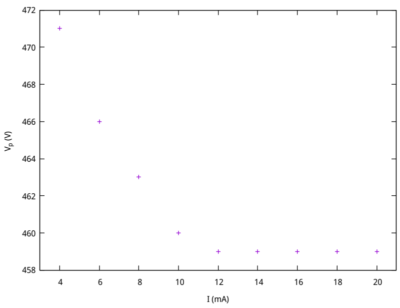


Figure 1: 0.39 mBar

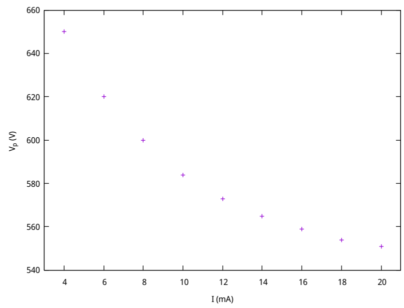


Figure 2: 0.9 mBar

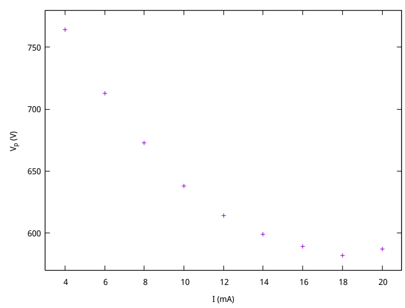


Figure 3: 1.3 mBar

Comparing figure 4 and figures 1 to 3 we can deduce that this corresponds to the normal glow region. Probably around the F point, implying that the gas just about broke down and is moving into the normal glow discharge regime with rising voltage, after which the voltage is almost independent of the current over several orders of magnitude in the discharge current.

4 Cas temperature calculations for all experimental conditions

To determine the gas temperature T_{gas} we require 3 quantities:

- α: A rotational term of the transition

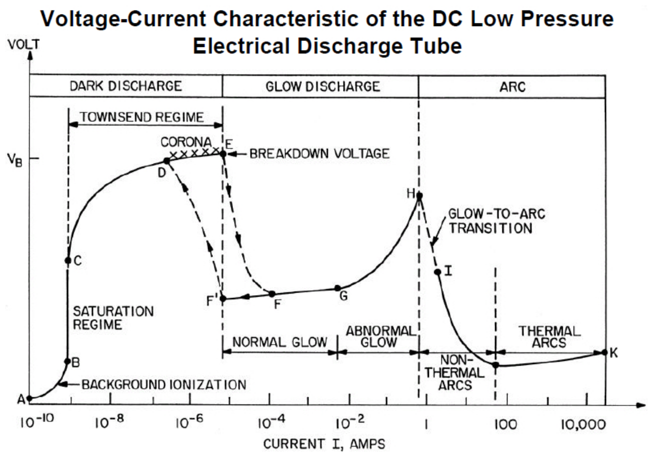


Figure 4: electric discharge regimes

$$\alpha = 1.4413 * F(J) = 1.4413 * [Bv * (J(J+1)) - Dv * (J(J+1))^2] \tag{7}$$

In which the rotational constant $Bv \approx B_e - \alpha_e(v + 0.5)$ with $\alpha_e = 0.0195$, $B_e = 2.083$. And $Dv = D_e + \beta_e(v + 0.5)$ with $\beta_e = 1.582 * 10^{-7}$, $D_e = 6.174 * 10^{-6}$. As our measurements will be of the 2-0 band (at 375-381), v=2.

- G: a rotational sum

$$G = 2(J+1)(J+2)/(2J+3) \tag{8}$$

- I: the measured intensity of the lines

We'll be using GNU octave to spline the data:

4.1 0.38 mBar

4.1.1 First measurement

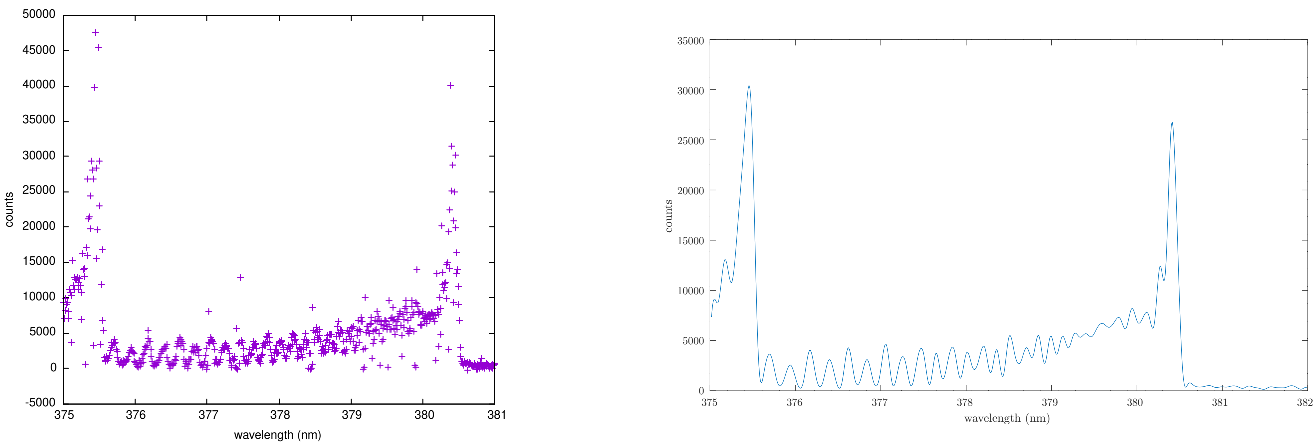


Figure 5: Frequency vs counts measurement for a 0.38 mBar plasma, left is a plot of the original data and right is the splined version (100 breaks)

To get an accurate temperature I'll be looking at a BREAK=200 spline shown in figure 6, the frequencies we're concerned with are in the range 375-381nm i.e 3750-3810 Å. If we take a look at "The Spectrum Of Molecular Nitrogen" [1] from this we can identify the following:

J number	G	α	counts
20	21.48837	1229.754	4133
19	20.4878	1112.779	4890
14	15.48387	615.295	5350
10	11.47826	322.4015	7500
8	9.473684	211.052	7400
5	6.461538	87.950	9600

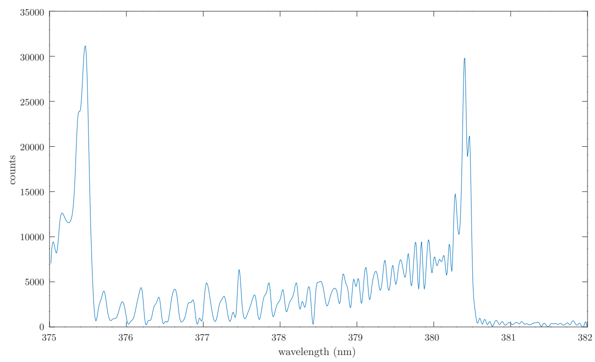


Figure 6: BREAK=200 splined data of a 0.38 mBar plasma

yielding a temperature of 606.65 ± 117K as shown in figure 7.

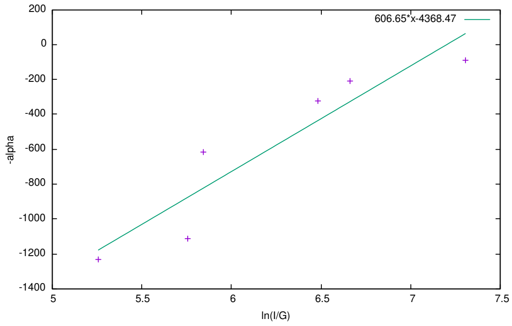


Figure 7: temperature fit on 0.38mbar plasma

J number	G	α	counts
20	21.48837	1229.755	4640
14	15.48387	615.2950	5580
8	9.473684	211.0524	7740
7	8.470588	164.1603	8205
6	7.466667	123.1258	9000
5	6.461538	87.95041	8900
4	5.454545	58.63550	11261

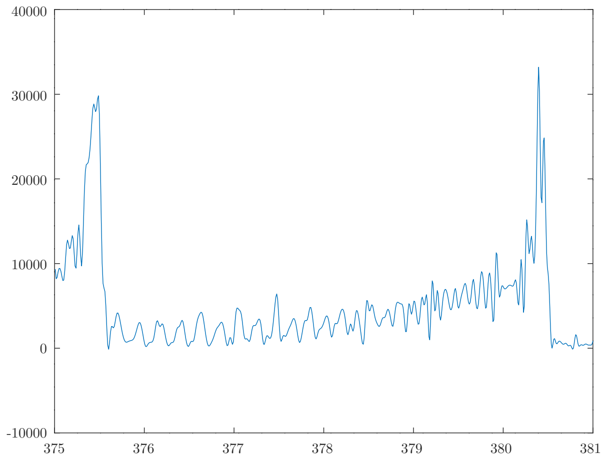


Figure 8: BREAK=200 splined data of a 0.38 mBar plasma

4.1.2 Second measurement

Completely analogous, but now focussing on low J for a wider spread of data:

yielding a temperature of 510.33 ± 82.07K as shown in figure 9.

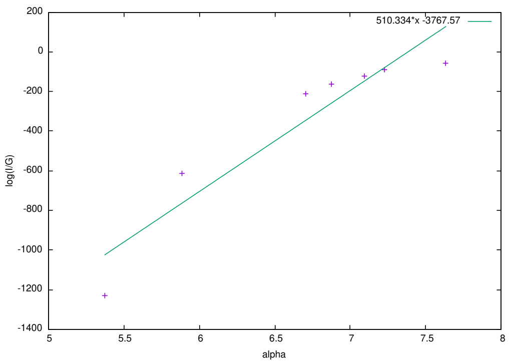


Figure 9: temperature fit on 0.38mbar plasma

So, taking the average of the two measurements, our gas is at a temperature of 558.49 ± 71.45K, where the error was estimated by using

$$\Delta y = \frac{1}{N}\sqrt{\sum_{i=1}^{N}(\Delta y_i)^2} \tag{9}$$

4.2 0.87 mBar

4.2.1 First measurement

J number	G	alpha	counts
4	5.4545	58.636	8915
6	7.4666	123.13	7016
8	9.4737	211.05	5850
14	15.483	615.30	4100
20	21.488	1229.8	3500

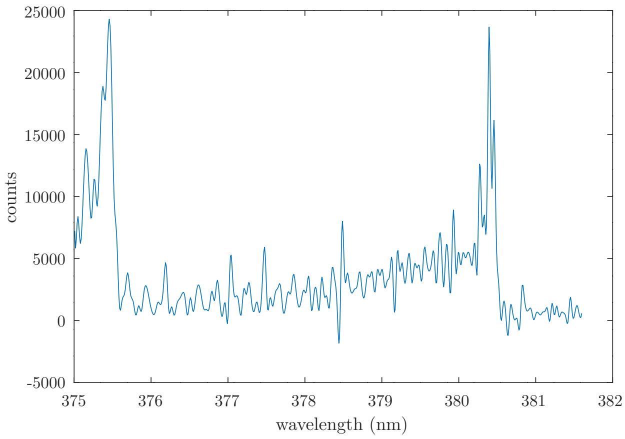
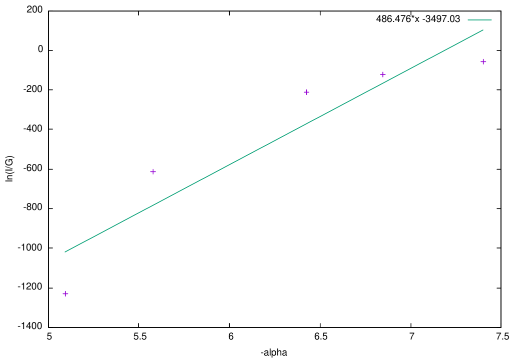


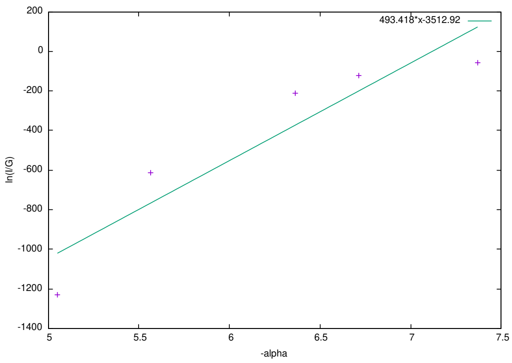
Figure 10: BREAK=200 splined data of a 0.87 mBar plasma



I.e a temperature of 486.476 ± 109.6K, the error is bigger as the data wasn't as clean.

4.2.2 Second measurement

Following a completely analogous method as the above treatment, we get:



I.e a temperature of 493.418 ± 114.3K, taking the average of the two we get 489.947 ± 79.178K.

4.3 1.3 mBar

4.3.1 First measurement

J number	counts	G	alpha
4	3500	5.455	58.636
6	2900	7.467	123.13
8	2830	9.474	211.05
14	2270	15.48	615.30
20	1370	21.49	1229.8

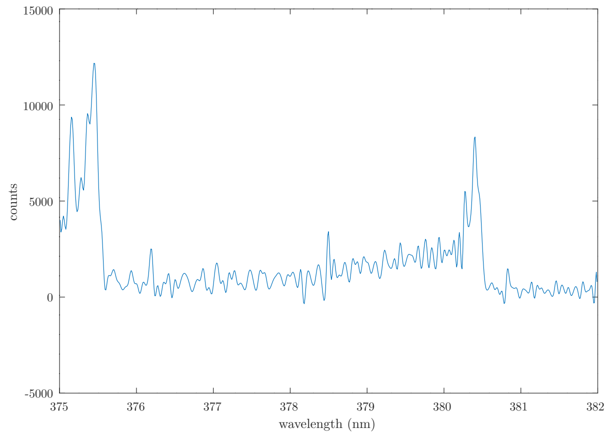
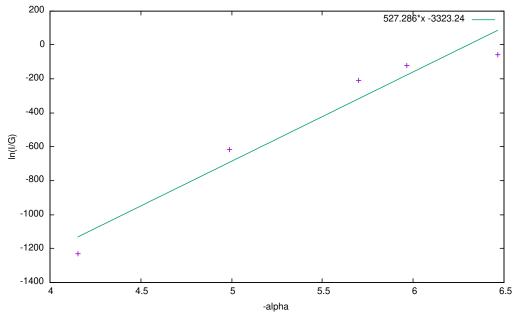


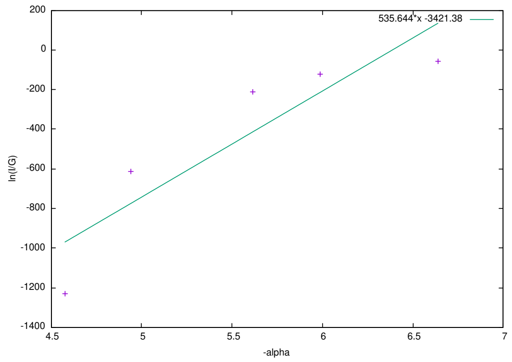
Figure 11: BREAK=200 splined data of a 1.3 mBar plasma

Yielding:



Giving a temperature of 527.286 ± 72.29K

4.3.2 Second measurement



Giving a temperature of 535.644 ± 149.1K, combining the two on average we get a temperature of 531.465 ± 82.85025K.

4.4 Dependence of gas temperature on discharge pressure

The results are shown in figure 12, the error on y is pretty big but we can see that we don't get the expected result of higher pressure $\rightarrow$ higher temperature. This difference might however still be due to measurement error, or the plasma wasn't in equilibrium as is required for the equations to hold.

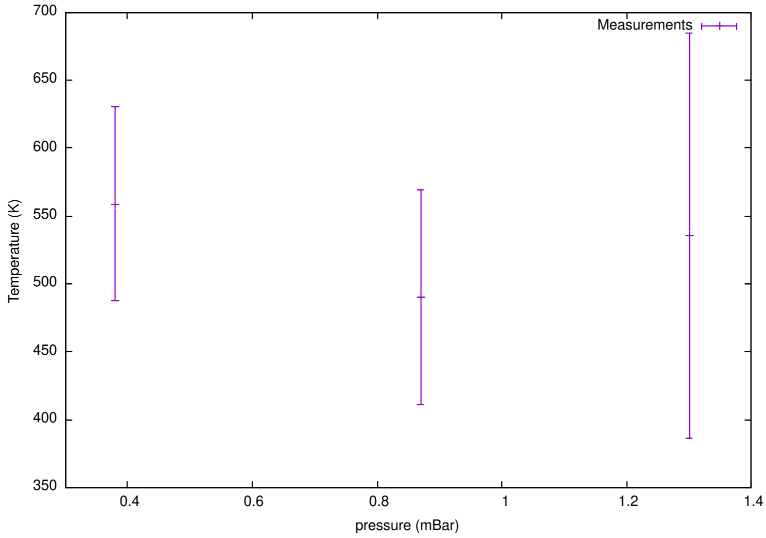


Figure 12: Temperature of the plasma vs pressure

References

[1] Alf Lofthus and Paul H. Krupenie. "The spectrum of molecular nitrogen". In: *Journal of Physical and Chemical Reference Data* 6.1 (1977), pp. 113–307. DOI: `10.1063/1.555546`. eprint: `https://doi.org/10.1063/1.555546`. URL: `https://doi.org/10.1063/1.555546`.