

Rydberg constant and emission spectra of gases

ONE WEIGHT

RECOMMENDED READINGS

1. R. Harris. Modern Physics, 2nd Ed. (2008). Sections 4.6, 7.3, 8.9.
2. Atomic Spectra line database https://physics.nist.gov/PhysRefData/ASD/lines_form.html

OBJECTIVE

- Calibrating a prism spectrometer to convert the scale readings in wavelengths of the emission spectral lines.
- Identifying an "unknown" gas by measuring its spectral lines wavelengths.
- Calculating the Rydberg constant R_H .
- Finding a separation of spectral lines in the yellow doublet of the sodium lamp spectrum.

INSTRUCTOR'S EXPECTATIONS

In the lab report it is expected to find the following parts:

- Brief overview of the Bohr's theory of hydrogen atom and main restrictions on its application.
- Description of the setup including its main parts and their functions.
- Description of the experiment procedure.
- Table with readings of the vernier scale of the spectrometer and corresponding wavelengths of spectral lines of hydrogen and helium.
- Calibration line for the function "wavelength vs reading" with explanation of the fitting procedure and values of the parameters of the fit with their uncertainties.
- Calculated Rydberg constant with its uncertainty.
- Description of the procedure of identification of the unknown gas and statement about the gas.
- Calculating resolution of the spectrometer with the yellow doublet of sodium spectrum.

INTRODUCTION

In this experiment, linear emission spectra of discharge tubes are studied. The discharge tube is an evacuated glass tube filled with a gas or a vapor. There are two conductors – anode and cathode - soldered in the ends of the tube and connected to a high-voltage power source outside the tube. High voltage applied between the anode and the cathode of the tube creates current of electrons (cathode rays) accelerated toward the anode. Collisions with atoms of a pure gas inside the discharge tube entail ionization of the atoms. Positively charged ions are moving to the cathode thus increasing the number of collisions among the particles in partially ionized plasma – a state of matter when electrons and ions coexist in a mixture and the number of electrons captured by the ions is equal to the number of electrons released due to ionization.

When an incident electron or an ion ionizes the neutral atom, the quantum state of the latter changes, the ion comes to the excited state with its total energy increased. Since the accelerated electron can create a vacancy at any electron shell in the atom, the plasma in the glow discharge contains ions at different energy states. The vacancy in either of the inner shell can be filled by one of the electrons of the outer electron shells of the ion. The electron transition is accompanied by emitting a photon and decreasing the ion energy. Thus, if we knew the energy of the two states participating in the transition, we could expect the energy of the emitted photon to equal the difference of the energies of the states. This modern understanding of discrete quantum states of an atom and the nature of photons, is based on genius contribution into quantum physics by Max Plank and Niels Bohr. The empirical Rydberg equation [Johannes Rydberg] and the Bohr's theory of atom result in the relationship between the energy of the emitted photon and the particular

electron transition between two states with principal quantum numbers m and n and energies T_m and T_n .

For the hydrogen atom, this gives:

$$hf = R_{EH} \left(\frac{1}{m^2} - \frac{1}{n^2} \right) = T_m - T_n \quad (1)$$

where R_{EH} is the Rydberg constant for hydrogen, and $R_{EH} = 13.605693 \text{ eV} = 2.179872 \times 10^{-18} \text{ J}$. T_m and T_n are called *terms*. The above conversion of energy units shows that the **electronvolt** (eV) is a very convenient unit and is widely used in particle, atomic and nuclear physics. The conversion from *electronvolts* (eV) to *joules* (J) is given by

$$1 \text{ eV} = 1.60218 \times 10^{-19} \text{ J}. \quad (2)$$

A formula similar to (1) was empirically obtained by Johann Balmer in 1885 for a visible spectrum of hydrogen as:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right), \quad (3)$$

where λ is the wavelength of the emitted line, n is the integer and $n > 2$. Unlike J. Balmer, we now know this integer as the principal quantum number of the state responsible for energy of the state.

Every photon has a specific energy

$$E_f = hf = hc / \lambda, \quad (4)$$

where $h = 6.626070040(81) \times 10^{-34} \text{ J}\cdot\text{s}$, is the Planck's constant; and c is the speed of light in vacuum. Thus, the Balmer formula (3) can be derived from the Eq.(1) by replacing the Rydberg constant R_{EH} , expressed in electronvolts, by the Rydberg constant R_H , expressed in the reciprocal of a unit of length. Conventionally accepted is the unit of cm^{-1} .

EQUIPMENT AND PREPARATION OF THE APPARATUS FOR MEASUREMENTS

The setup (Fig.1 and 2) consists of a tri-prism spectrometer with calibrated constant λ_0 ; a set of discharge tubes with different gases and the power supply for the tube; and a sodium lamp and power supply for it.

The spectrometer is capable of resolving to about 0.1 nm. The instrument reads the wavelength of the light in arbitrary units. A calibration chart is required to convert scale readings to wavelengths. The visible spectrum is contained in 20 of the 50 divisions, with resolution by the vernier to 0.01 divisions. Setting of the instrument is accomplished by aligning a cross-hair precisely on an image of the spectral line seen in the eyepiece.

To get a clear image of the linear spectrum, you have to first adjust the slit width and focus the eyepiece. Turn on a sodium lamp power supply and wait until the color of the light becomes yellow.

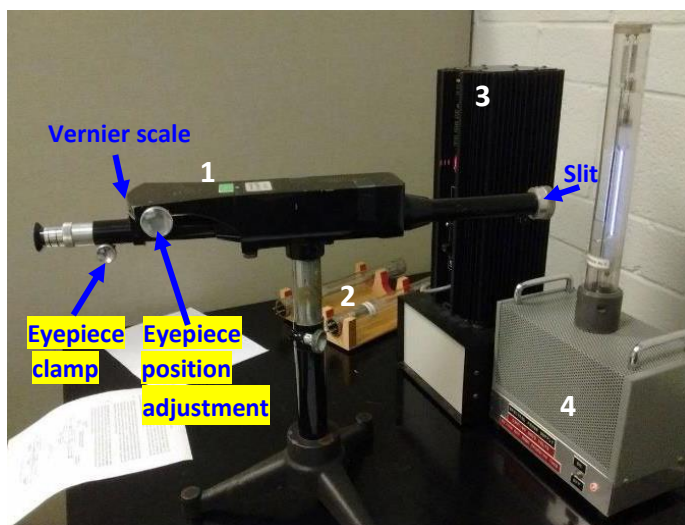


FIG.1: Rydberg constant experiment station:
 1 – spectrometer with prism housing;
 2 – set of discharge tubes;
 3 – sodium lamp;
 4 – power supply for the discharge tube

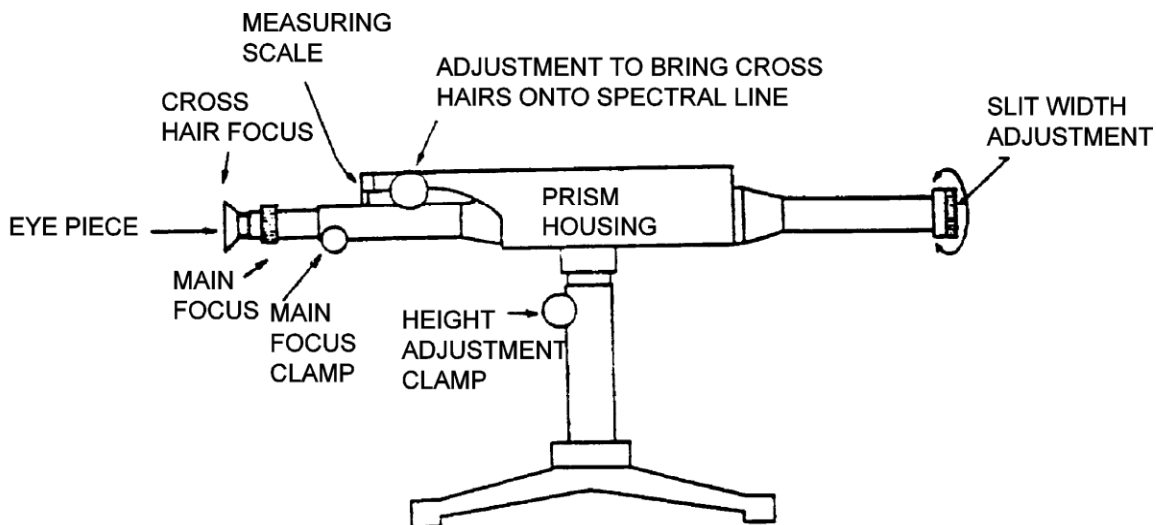


FIG. 2.

Looking into the eyepiece and slowly rotating the eyepiece position adjustment knob, find the bright yellow double line. Focus the spectrometer optics on the spectral line by moving the eyepiece assembly in or out of the black main frame with the knurled knob. Reduce the slit width until the sodium line resolves into two. (Refocus if necessary). When the line is clearly focused, tighten the focusing clamp. The paint dot on the slit adjustment should be kept on the upper side of the spectrometer to maintain calibration. The spectrometer is now ready for use.

When observing spectra, the slit may be opened or closed, as desired. Opening the slit will increase the brightness but decrease the resolution.

Measure the wavelength of lines by precisely splitting the line with the centre of the cross hairs, and then reading the scale and vernier (see APPENDIX 1 for a guide in the Vernier measurements).

When making observations in the violet it may be necessary to slightly push in the eyepiece in order to keep the cross-hairs in focus.

PROCEDURE

1. CALIBRATION WITH THE HARTMANN RELATION METHOD

Calibrating the spectrometer means determining the relationship between the wavelength λ of a spectral line and the scale reading y on the instrument. Once this relationship is obtained, you can use it to convert the scale reading of an unknown line to the corresponding wavelength. Use the helium and hydrogen lamps and the tables from Appendix 2 to calibrate the spectrometer using the Hartmann relation method outlined below.

The relationship between the scale reading y and the wavelength λ is given by the Hartmann dispersion relation as follows:

$$y = \frac{m}{\lambda - \lambda_0} + b \quad (5)$$

where λ_0 , m and b are constants.

For your convenience, the constant λ_0 , which is a function of the optics of your spectrometer, has been measured for each spectrometer and is marked on the top of the instrument. By plotting y

vs. $(\lambda - \lambda_0)^{-1}$, a straight line can be obtained, and m and b can be estimated. The advantage of this method is that since the calibration curve is a straight line, you need fewer calibration points, it is easier to draw and it is more accurate.

The recommended spectral lines of helium and hydrogen for calibration are given in Table 1. Plug in a tube with He into the power supply and turn it on. Find the strongest lines in the spectrum of helium and fill the Table 1 for this element. Turn off the power supply, replace the tube with helium by the tube with hydrogen and repeat the procedure.

Table 1. Data for λ 's are taken from https://physics.nist.gov/PhysRefData/ASD/lines_form.html

	Helium strong lines						Hydrogen strong lines			
λ , nm	447.1	471.3	492.2	501.6	587.6	667.8	410.2	434.0	486.1	656.3
Color	Blue	Blue	Blue	Cyan	Yellow	Red	Violet	Violet	Blue	Red
y										

Fill in the cells for the spectrometer readings y and perform fitting. Show the diagram with the fitting function and the data points with their error bars. Calculate the constants m and b for the Eq. (5) with their uncertainties.

2. IDENTIFICATION OF THE UNKNOWN GAS

Replace the calibration gas tube by the tube with the unknown gas. Prepare a table, similar to the Table 1, for the lines you can observe in the unknown gas spectrum. Compare your data with the spectra in Fig.3 and make a guess about the unknown substance in the discharge tube.

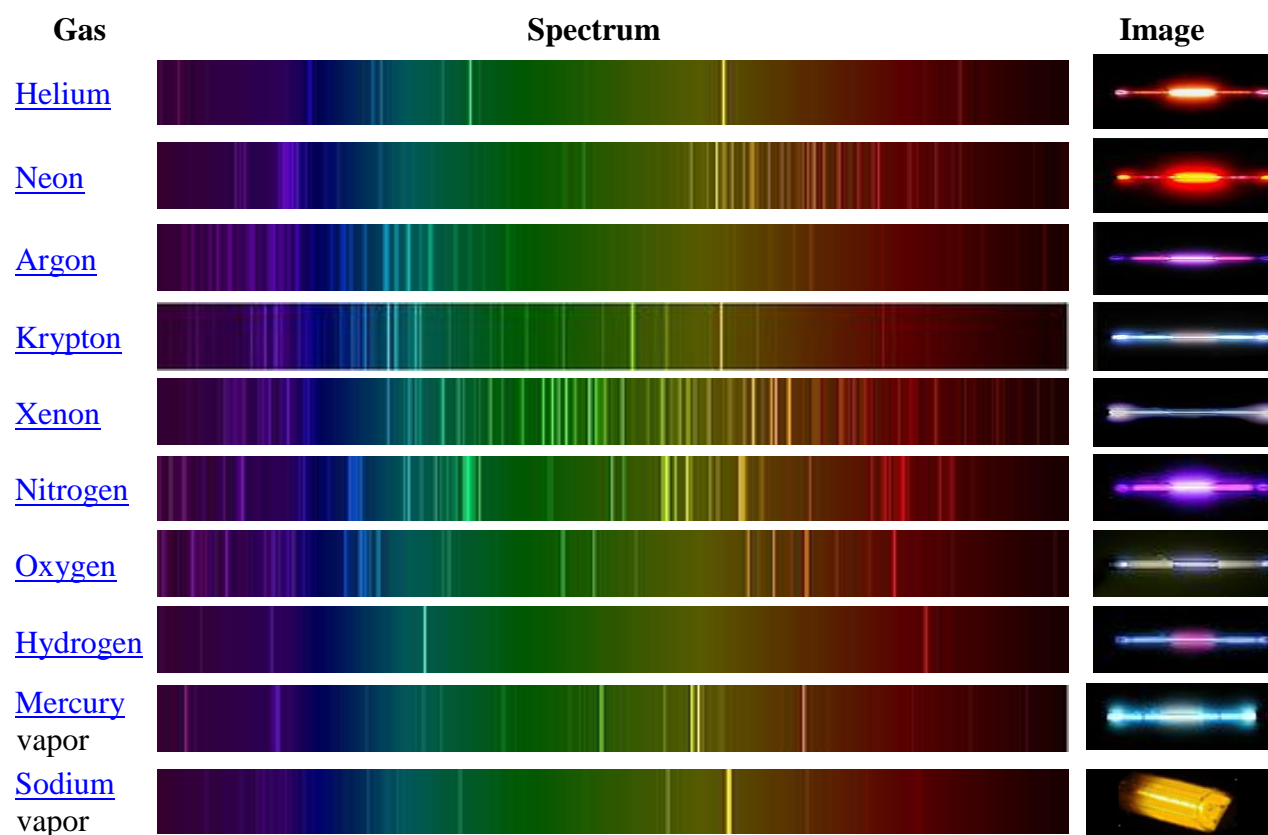


FIG. 3: Emission spectra of gases and vapors under low pressure. The data taken from https://en.wikipedia.org/wiki/Gas-discharge_lamp#Color

calibration function for measured readings y_i , calculate the wavelengths λ_i of the observed spectral lines. With the data from APENDIX 2 and considering the Fig.3, conclude on the nature of the unknown gas.

3. THE RYDBERG CONSTANT

- Apply Eq. (3) to the wavelengths of the spectral lines of hydrogen and calculate the Rydberg constant R_H .
- With Eqs. (1) and (4) convert the R_H into R_{EH} in electronvolts.
- Compare your result to the given value on p. 2 under Eq. (1). Discuss the result.
- Compare it to the ionization energy of atomic hydrogen.
- What is the physical significance of R_{EH} ?

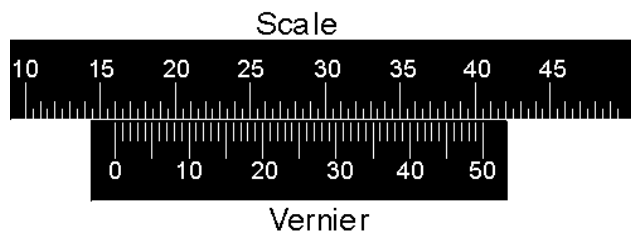
4. CALCULATING THE SEPARATION OF SPECTRAL LINES IN THE YELLOW DOUBLET OF SODIUM.

Turn off the power supply for the discharge tubes and turn on the sodium lamp. Wait a bit for the lamp to warm up. When the color of the discharge becomes yellow, measure the separation of the two yellow lines and express it in nm, cm^{-1} and eV.

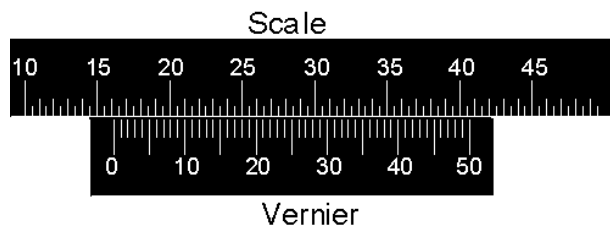
The yellow doublet of sodium is being used for adjusting optical devices to the best possible resolution. If the device detects these two lines separately, this is a good resolution. The tabulated wavelengths of the lines of the yellow doublet are 588.9950 nm and 589.5924 nm. Using your calibration parameters from part 1 of this experiment, find the wavelengths of the two yellow lines in the spectrum of sodium vapor. Conclude on the accuracy of measurements with the spectrometer in this experiment and accuracy of calibration you performed in part 1.

APPENDIX 1. Examples with reading the vernier scale on the spectrometer. Taken from <https://faraday.physics.utoronto.ca/IYearLab/Intros/Spectra/Spectra.html>

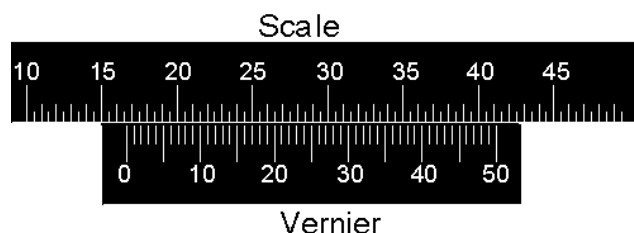
The vernier has only 50 divisions. Remember to add 50 to the vernier reading when the point is in the second half of a main division.



In the above diagram the "pointer" of the vernier, the line labeled with 0, lines up almost exactly with the 16th division of the scale. The units of the scale are arbitrary so the reading is 16.00 units. However, notice that the vernier goes from 0 to 50 instead of 0 to 100.



Now the pointer is between 16.00 and 16.50 units. The 15 line on the vernier lines up almost exactly with a line on the scale, so the reading is $16.00 + 0.15 = 16.15$ units.



Now the pointer is between 16.50 and 17.00 units, and again the 15 line on the vernier lines up almost exactly with a line on the scale. So, in this case the reading is $16.50 + 0.15 = 16.65$ units.

APPENDIX 2. Tables of spectral lines and their wavelengths.

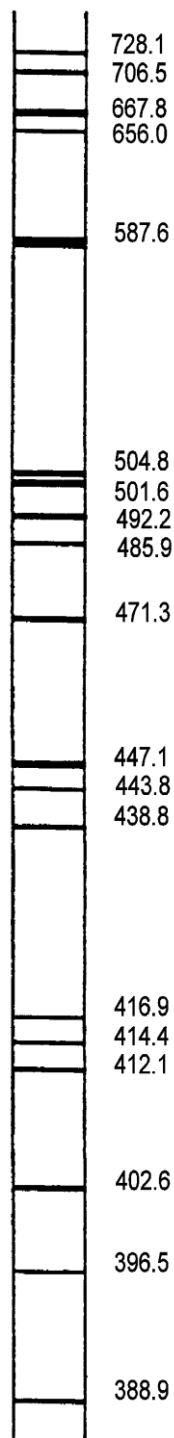
You may use the tables with more up-to-date data on the web site https://physics.nist.gov/PhysRefData/ASD/lines_form.html

Remarks on the use of the tables

- 1) Use the intensity indications with caution. They are meant only as a general guide. Relative intensities vary widely depending on the mode of excitation and so the source that you are using may have lines with different intensities. However, the very bright lines should appear bright in all sources.
- 2) These tables give most of the lines that you will be able to see (and many that you won't be able to see if you are using a narrow-slit width). However, the tables are not complete and lack some faint lines.
- 3) Lines separated by less than one nanometer will not be resolved if the slit is wide. If the slit is too narrow, weak lines won't be seen.
- 4) You may assume that the errors in these values are negligible in comparison to the other errors in this experiment.

HELIUM

WAVELENGTH <i>nm</i>	RELATIVE INTENSITY	COLOUR
728.1	2	RED
706.5	4	RED
667.8	6	RED
656.0	1	RED
587.6	10	YELLOW
504.8	4	GREEN
501.6	6	GREEN
492.2	5	GREEN
485.9	2	GREEN
471.3	5	BLUE
447.1	6	BLUE
443.8	1	VIOLET
438.8	4	VIOLET
416.9	1	VIOLET
414.4	2	VIOLET
412.1	3	VIOLET
402.6	4	VIOLET
396.5	1	VIOLET
388.9	3	VIOLET



RED

WAVELENGTH - nanometres (nm)



VIOLET

ARGON

<i>WAVELENGTH</i> <i>nm</i>	<i>RELATIVE</i> <i>INTENSITY</i>	<i>COLOUR</i>
574.0	2	GREEN
565.0	3	GREEN
560.7	3	GREEN
557.3	3	GREEN
549.6	3	GREEN
522.1	2	GREEN
518.8	3	GREEN
516.2	3	GREEN
470.2	1	BLUE
462.8	1	BLUE
459.6	1	BLUE
452.2	1	VIOLET
451.1	2	VIOLET
433.5	2	VIOLET
433.4	2	VIOLET
430.0	3	VIOLET
426.6	3	VIOLET
425.9	3	VIOLET
420.1	2	VIOLET
419.8	2	VIOLET
416.4	3	VIOLET
415.9	2	VIOLET

KRYPTON

<i>WAVELENGTH</i> <i>nm</i>	<i>RELATIVE</i> <i>INTENSITY</i>	<i>COLOUR</i>
645.6	5	RED
642.1	5	RED
605.6	2	RED
601.	2	ORANGE
599.	2	ORANGE
588.	1	ORANGE
587.	10	ORANGE
584.	1	YELLOW
583.	1	YELLOW
570.	1	GREEN
567.	1	GREEN
565.	1	GREEN
558.	1	GREEN
557.	10	GREEN
556.	2	GREEN
450.	5	VIOLET
446.	5	VIOLET
445.	5	VIOLET
440.	2	VIOLET
437.	5	VIOLET
436.	4	VIOLET
432.	3	VIOLET
431.	2	VIOLET
427.	5	VIOLET

Argon has many faint lines in the red and yellow which vary in intensity depending on the source and because of the confusion that this can lead to only wavelengths less than 580 nm are given. In this region there are a very large number of lines. Only relatively brighter ones are listed. Fainter ones may provide a haze in the background.

MERCURY**XENON**

<i>WAVELENGTH</i> <i>nm</i>	<i>RELATIVE</i> <i>INTENSITY</i>	<i>COLOUR</i>	<i>WAVELENGTH</i> <i>nm</i>	<i>RELATIVE</i> <i>INTENSITY</i>	<i>COLOUR</i>
708.2	1	RED	647.3	2	RED
704.5	2	RED	647.0	3	RED
690.7	1	RED	631.8	5	RED
671.6	1	RED	620.1	1	RED
658.5	1	RED	619.8	1	RED
638.3	2	RED	618.2	3	RED
623.4	2	RED	618.0	1	RED
612.3	2	RED	617.8	2	RED
607.3	2	ORANGE	616.4	1	RED
602.4	2	ORANGE	593.4	2	ORANGE
601.7	1	ORANGE	593.1	1	ORANGE
589.0	1	YELLOW	589.5	2	ORANGE
579.1	8	YELLOW	587.5	1	ORANGE
577.0	6	YELLOW	582.5	2	YELLOW
567.7	1	YELLOW	582.4	3	YELLOW
567.6	1	YELLOW	571.6	1	YELLOW
546.1	10	GREEN	569.7	1	YELLOW
536.5	1	GREEN	569.6	1	YELLOW
520.5	1	GREEN	546.0	1	GREEN
519.6	1	GREEN	539.3	1	GREEN
512.1	1	GREEN	502.8	3	GREEN
504.6	1	GREEN	492.3	4	GREEN
502.6	1	GREEN	491.7	4	GREEN
496.0	1	GREEN	484.3	4	GREEN
491.6	5	BLUE	483.0	4	GREEN
452.3	1	BLUE	480.7	5	GREEN
435.8	6	VIOLET	479.3	1	BLUE
434.8	2	VIOLET	473.4	5	BLUE
433.9	1	VIOLET	469.7	4	BLUE
421.2	1	VIOLET	467.1	10	BLUE
420.6	1	VIOLET	462.4	5	BLUE
415.7	1	VIOLET	458.3	1	VIOLET
407.8	5	VIOLET	452.5	2	VIOLET
414.7	5	VIOLET	450.1	2	VIOLET

<u>NEON</u>			<u>NITROGEN</u>		
WAVELENGTH <i>nm</i>	RELATIVE INTENSITY	COLOUR	WAVELENGTH <i>nm</i>	RELATIVE INTENSITY	COLOUR
724.5	1	RED	497.6	3	GREEN
717.4	1	RED	491.7	3	GREEN
703.2	5	RED	481.5	3	GREEN
702.4	3	RED	472.4	3	BLUE
692.9	6	RED	466.7	3	BLUE
667.8	7	RED	464.9	3	BLUE
659.9	7	RED	457.4	3	BLUE
653.3	7	RED	449.0	3	BLUE
650.7	7	RED	441.7	3	VIOLET
609.6	5	ORANGE	435.5	3	VIOLET
607.4	7	ORANGE	434.4	2	VIOLET
603.0	5	ORANGE	427.0	2	VIOLET
596.5	4	ORANGE	420.1	2	VIOLET
588.2	6	YELLOW	414.2	2	VIOLET
585.2	10	YELLOW	409.5	1	VIOLET
540.1	5	GREEN	406.0	1	VIOLET
			399.8	1	VIOLET
			394.3	1	VIOLET

Many orange and yellow lines have been omitted as well as lines of wavelength less than 540 nm (hundreds). Most of these are faint but some overlap to give the appearance bright lines.

Since **nitrogen** is a molecule, the all spectrum consists of bands rather than lines. This is due to rotation of the molecules. In the visible the most prominent structure is the First Positive of series with about 30 regularly spaced bands in the region 500- 700 nm. Only the band heads of the Second Positive series are tabled above. The bands trail off to shorter wavelengths. As indicated by the relative intensities on a scale of 10, the Second Positive series is less intense than the First Positive series.