

Spectrometry and Rydberg's constant

Phys 294/5 Experiment 5

Instructor's manual

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1 Theory ¹

This experiment uses spectroscopy to extract information about what the composition of gases based on their emission light spectra. Spectroscopy was used back in the 19th century to find the existence of helium. This was done by looking at the absorption line spectrum from the Sun. (More to come.) Both processes are evidence of the quantum nature of matter, and of the particle-wave duality of light.

Atoms have electrons orbiting around their nucleus, with the electrons occupying orbits that correspond to determined amounts of energy. These amounts of energy follow a ladder pattern, i.e. the energy levels are not continuous throughout the orbits, but quantized. This quantization is unique for each element of the periodic table. This means that knowing the quantization of energy from the atoms of an 'unknown' gas can tell you of which element the gas is made of. The observation of the quantized energy levels can be performed, indirectly, in two ways: by supplying energy to the gas in order to excite and subsequently de-excite the atoms' electrons to obtain an emission spectrum (see Figure 1b), or to shine a continuous spectrum (i.e. a spectrum without any absorption lines; see Figure 1a) through the gas to obtain an absorption spectrum (see Figure 1c).

¹Based on *The cosmic perspective* [3] and Carter [2]

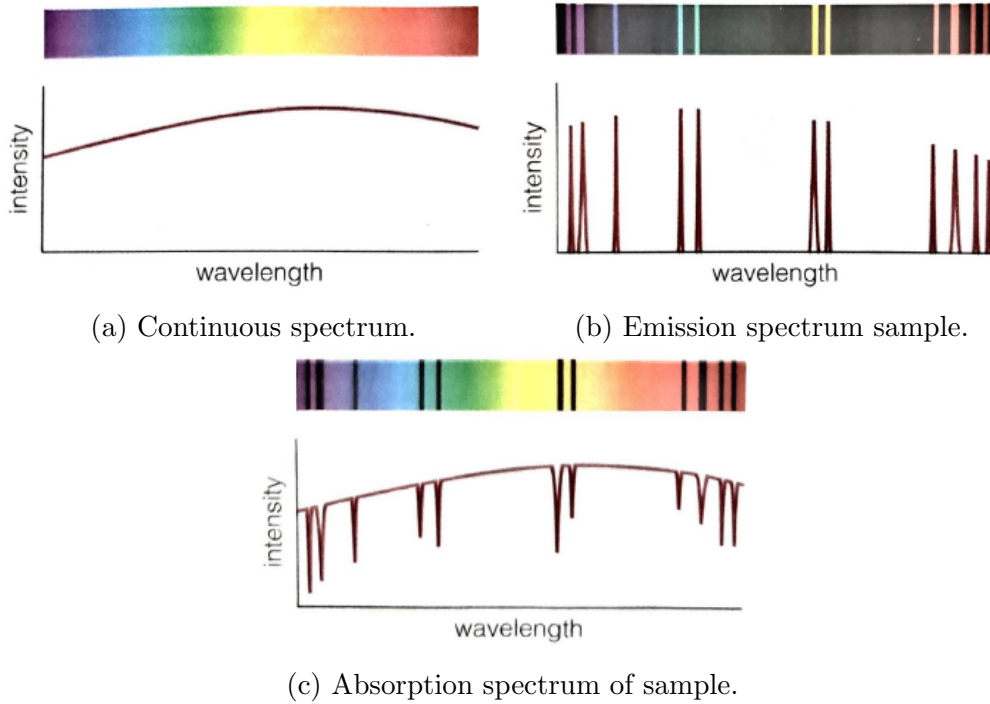


Figure 1: Sample spectra. Taken from *The cosmic perspective* [3], Figure 5.14.

The process behind emission of light in a gas is the following: atoms colliding in a cloud of gas continually transfer energy to each other. Sometimes this energy is enough to excite the electrons of the atoms to their different orbit levels. Continually supplying energy to the cloud of gas will cause these just right excitations to occur more often. But the electrons tend to fall back to lower energy levels, specially the ground state energy level, very quickly, losing an amount of energy equal to the difference between the energies corresponding the the two subsequent occupied orbits. This energy is lost by the emission of a photon.

Now, the Plank-Einstein relation says that the energy of a photon (or light packet) is directly proportional to the frequency of the photon:

$$E = h\nu \quad (1)$$

So the photons emitted will have frequencies corresponding to the difference in energy levels of the atoms' orbits. No other photons with other frequencies could be seen. Figure 2 shows the emission spectrum of hydrogen for visible light frequencies.

The process behind absorption of light in a gas is very similar. This time,

light is shone through the gas and the electrons of the gas' atoms absorb photons with frequencies corresponding to the differences in energy of the atoms' orbits. So, when looking at such a gas cloud through a spectrometer, you would see a continuous spectrum. Now, if you put a gas in front of the light source, you would see dark lines in the once continuous spectrum. Figure 1c shows the absorption spectrum of a sample gas. Notice that the bright lines from Figure 1b and the dark lines of Figure 1c are exactly in the same place on the spectrometer scale.

1.1 Rydberg's constant

In the early 20th century, Niels Bohr (1885-1962) proposed what is known as the Bohr model of the atom: an electron orbiting the nucleus in orbits/radii with corresponding quantized energies, much like a solar-system-like model of the atom. From his proposition of quantization, the following relation for the hydrogen atom is derived (more on this later):

$$E_n = \frac{E_1}{n^2}, n = 1, 2, 3, \dots, \quad (2)$$

where E_n is the energy of the n th orbit of the Hydrogen atom. So a transition of an electron from an energy level E_j to E_i can be written as:

$$\Delta E = E_1 \left(\frac{1}{j^2} - \frac{1}{i^2} \right). \quad (3)$$

This means that the emitted photon will have an energy

$$\Delta E = E_1 \left(\frac{1}{j^2} - \frac{1}{i^2} \right) = h\nu. \quad (4)$$

The ground state of the hydrogen atom has a corresponding energy value of -13.6 eV. Using Equation 2 one can calculate the energy levels of the hydrogen atom; these are shown in Table 1.

Energy [eV]	Quantum number, n
-13.6	1
-3.40	2
-1.51	3
-0.850	4
-0.544	5

Table 1: Energy levels of the Hydrogen atom. The ionization level is not included.

But light is also a wave!, so $c = \lambda\nu$, where λ is the wavelength of the light and c is the speed of light. This gives us the following equation, defining $R \equiv \frac{E_1}{hc}$:

$$\frac{1}{\lambda} = R\left(\frac{1}{j^2} - \frac{1}{i^2}\right), \quad (5)$$

where R is called Rydberg's constant. For completeness purposes we now derive Equation 2 using classical mechanics, as Bohr did himself.

The energy of an electron orbiting the nucleus of a hydrogen atom is given by

$$E = T + V = \frac{1}{2}mv^2 - k\frac{e^2}{r}, \quad (6)$$

which is just the sum of the kinetic and potential energies of the electron. m is the mass of the electron, v is the speed of the electron. For the potential energy, we have used Coulomb's law. e is the elementary charge unit and r is the radius of the electron's orbit with respect to the nucleus. k is Coulomb's constant.

The angular momentum of the electron is given by $L = mvr$, and if we quantize it, we obtain:

$$L = mvr = C \times n, n = 1, 2, 3, \dots \quad (7)$$

The constant C here needs to have units of angular momentum. At the end of the experiment you can verify that $C = \frac{h}{2\pi}$. Squaring:

$$m^2v^2r^2 = C^2n^2, \quad (8)$$

or

$$mv^2 = \frac{C^2n^2}{mr^2}. \quad (9)$$

But the force between the electron and the nucleus is centripetal, and it equals Coulomb's force!, so

$$F = m\frac{v^2}{r} = k\frac{e^2}{r^2}, \quad (10)$$

which simplifies to

$$mv^2 = k\frac{e^2}{r}. \quad (11)$$

We conclude two things: 1) that the kinetic energy of the electron can be expressed as

$$T = \frac{1}{2}k\frac{e^2}{r}, \quad (12)$$

which implies that the total energy of the electron is

$$E = -\frac{1}{2}k\frac{e^2}{r}, \quad (13)$$

and 2), comparing Equations 9 & 11, that

$$\frac{C^2n^2}{m} = ke^2r, \quad (14)$$

which, solving for r and plugging into Equation 13, implies that the energy levels of the electron in the hydrogen atom are quantized:

$$E = -\frac{1}{2}k\frac{e^2}{\frac{C^2n^2}{mke^2}} = -\left(\frac{mk^2e^4}{2C^2}\right)\frac{1}{n^2} = \frac{E_1}{n^2}, n = 1, 2, 3, \quad (15)$$

There are several problems, as you might have suspected, or noticed, with this derivation. One of them for example is that we are ignoring the synchrotron radiation of the electron as it orbits the nucleus, which would require the electron to fall down towards the center of the atom in a spiral. See Ford [5] for a discussion on this. The original derivation as presented by Bohr can be found in his 'trilogy' [1]. A (more appropriate) derivation of this equation using quantum mechanics is possible, but too advanced for this course; however, if you are interested in studying the quantum mechanical derivation, see Griffiths [4], Chapter 4.

2 Experimental details

In this experiment, you will calculate Rydberg's constant for hydrogen using Figure 2. This picture of the emission spectrum was taken with the spectrometer provided for this experiment. You will also look at different light sources available to you to determine the elements used in the lamps you look at.

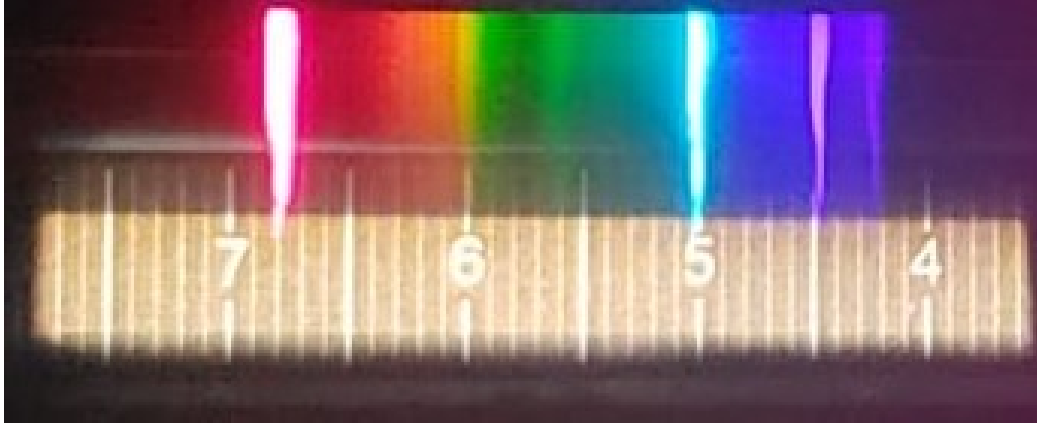


Figure 2: Hydrogen emission spectrum.

Rydberg's constant for hydrogen can be found experimentally through linearisation techniques. Recall the formula (Equation 5), now modified for obtaining a positive R (this is because in Equation 5 we defined $R \equiv \frac{E_1}{hc}$, $E_1 < 0$):

$$\frac{1}{\lambda} = R\left(\frac{1}{i^2} - \frac{1}{j^2}\right). \quad (16)$$

For the hydrogen atom, transitions for $i = 1$ are not in the visible spectrum, so we will ignore those cases, which are not seen with the naked eye through the spectrometer. So consider the lowest $i = 2$. You can obtain λ from the spectrometer and i and j from the order of the emission lines. Remember that $c = \lambda\nu$ implies that higher energy photons correspond to shorter wavelengths. R can be obtained from the slope of a line with $\frac{1}{\lambda}$ values in the vertical axis and $(\frac{1}{i^2} - \frac{1}{j^2})$ in the horizontal axis. Finally, using Equations 5 & 15 corroborate that $C = \frac{h}{2\pi}$.

Table 2 shows the wavelengths of the emission lines of hydrogen determined from Figure 2. (All the uncertainties can be found in the attached Excel document.) Table 3 shows the results from linearising the data on Table 2 according to Equation 16, with R , Rydberg's constant being determined from the slope of the linear least-squares weighted fit.

Wavelength [nm]	$\frac{1}{2^2} - \frac{1}{n^2}$
680	$\frac{1}{2^2} - \frac{1}{1^2}$
500	$\frac{1}{2^2} - \frac{1}{3^2}$
450	$\frac{1}{2^2} - \frac{1}{5^2}$

Table 2: Experimental data.

	Rydberg's constant [m^{-1}]	uncertainty [m^{-1}]
Experimental value	1.07×10^7	0.06×10^7
Accepted value	1.097×10^7	0.002×10^7

Table 3: Results data.

Define the reduced Plank constant $\hbar \equiv \frac{h}{2\pi} = 1.054571817 \times 10^{-34} \text{ J s}$ (exact value). Using $R \equiv \frac{|E_1|}{hc}$ (Equation 5, for a positive value of R) and $|E_1| = \frac{mk^2e^4}{2C^2}$, one concludes that $C = \sqrt{\frac{mk^2e^4}{2hcR}}$. Plugging in the values of the constants ², we conclude that (all calculations included in the attached Excel document) $C = \hbar = 1.07 \pm 0.06 \times 10^{-34}$. The accepted value is ³ $\hbar = 1.05457(\text{exact}) \times 10^{-34}$.

For the sources of light available to you, focus on the differences between energy levels of the elements you suspect the lamp contains. Keep in mind which if these differences correspond to the emission of a photon in the visible range, and which not.

Notes: in order to show that you performed the experiment, you are required to take a picture of the spectra that you analysed. The apparatus is neither very precise nor very accurate, and placing the camera at an angle through the small slit does not help with the situation either. This is not a problem for the determination of the Rydberg constant of the hydrogen atom, but it is a problem for the rest of the experiment consisting of identifying the elements used in the sources of light you observe. It is very important then to focus on the **energy differences** between the allowed energy levels of the elements. Appendix A contains the emission spectra of different elements available in the laboratory; you can use these to determine the differences in energy levels, and to compare with the emission spectra you observe from the sources of light available to you. The correct way of reading the scale in the spectrometer is the following: a line about the number 6 means a

²From NIST.

³From NIST.

wavelength of 600 nm. Finally, if you do not feel comfortable going out of your house to look at sources of light ⁴, **please** talk to your TA, you will **not** be penalized in any way. A good place to access the values of constants and important quantities is the web page of the National Institute of Standards and Technology. ⁵

References

- [1] Bohr, N. II. The trilogy: on the constitution of atoms and molecules. Niels Bohr collected works. Editor: L. Rosenfeld, Ulrich Hoyer, Elsevier, Volume 2, 1981, pp. 159-233. doi: [https://doi.org/10.1016/S1876-0503\(08\)70046-X](https://doi.org/10.1016/S1876-0503(08)70046-X). For the entire collection: <https://www.sciencedirect.com/bookseries/niels-bohr-collected-works/vol/2>.
- [2] Carter, R. Derivation of Bohr's Equations for the One-electron Atom. Chemistry 115: Chemical principles I. The University of Massachusetts Boston. Retrieved from (Aug. 3, 2020): <http://alpha.chem.umb.edu/chemistry/ch115/carter/>; <http://alpha.chem.umb.edu/chemistry/ch115/carter/files/103more/BohrEquations.pdf>
- [3] Bennett, J. O.; et al. (2017). The cosmic perspective. 8th ed. Pearson.
- [4] Griffiths, D. (2005). Introduction to quantum mechanics. 2nd ed. Pearson Prentice Hall.
- [5] Ford, K. W. (2018). Niels Bohr's first 1913 paper: still relevant, still exciting, still puzzling. The Physics Teacher 56, 500. <https://doi.org/10.1119/1.5064553>.

⁴Specially during these times, with the COVID-19 pandemic happening.

⁵Link: <https://physics.nist.gov/cuu/Constants/index.html>.

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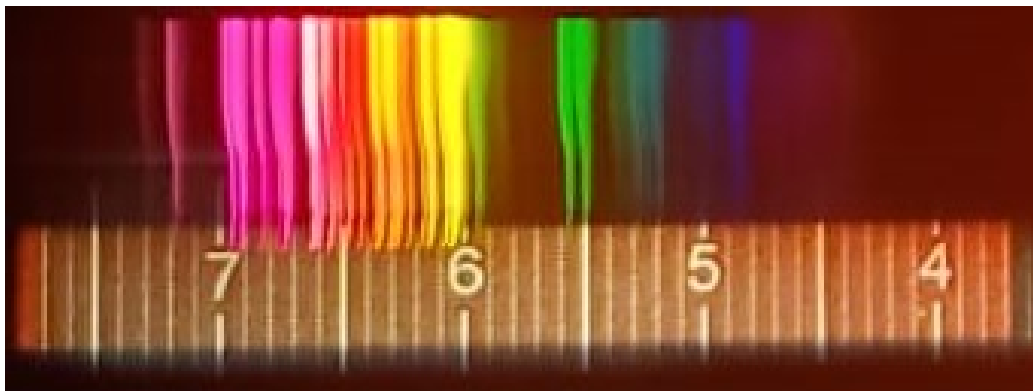


Figure 3: Neon emission spectrum.

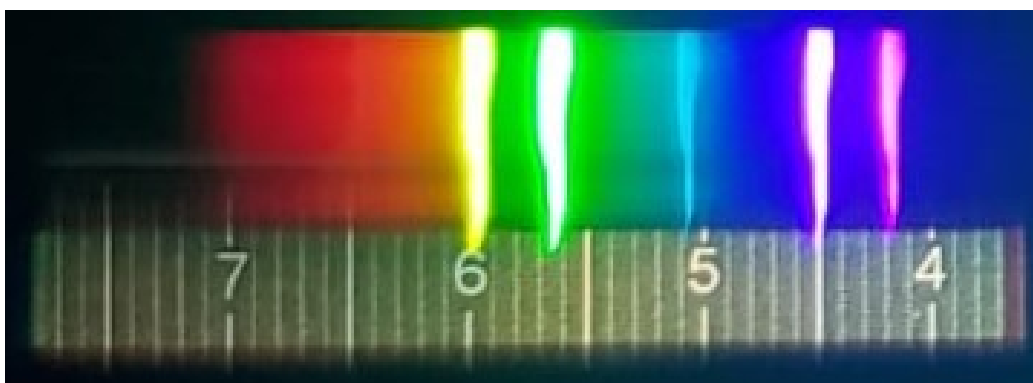


Figure 4: Mercury emission spectrum.

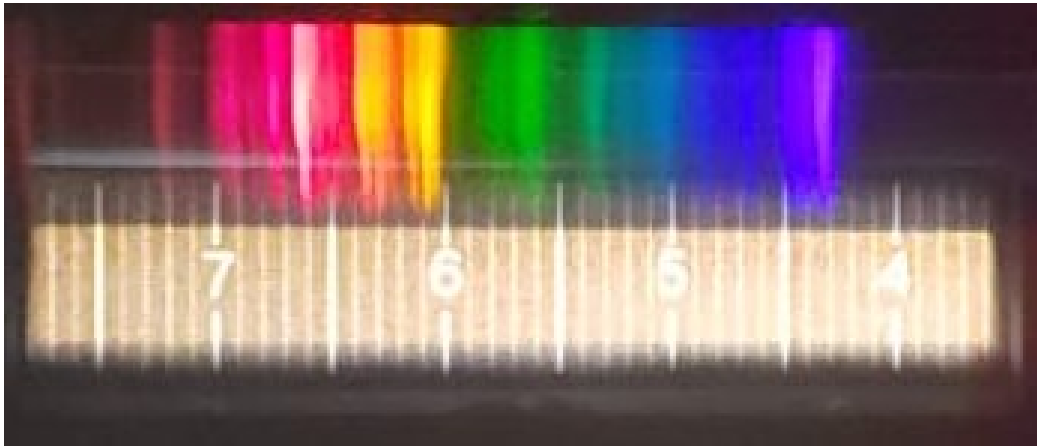


Figure 5: Sodium emission spectrum.

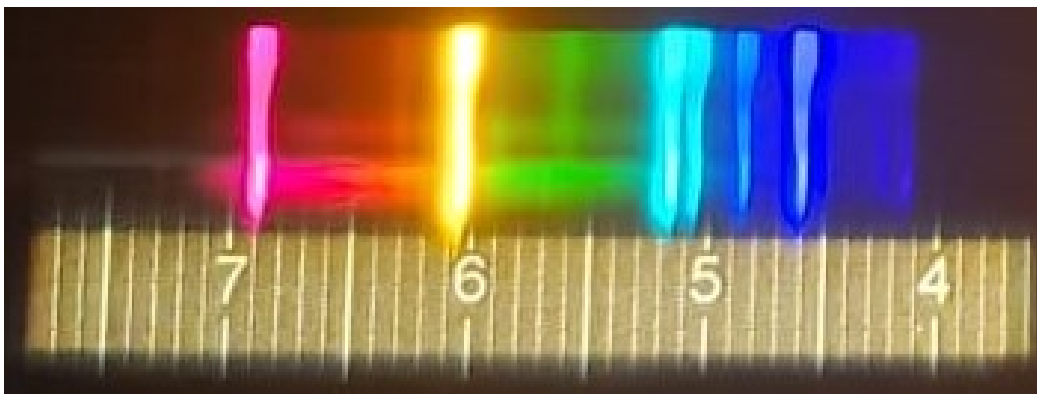


Figure 6: Helium emission spectrum.