The atomic emission spectra of hydrogen and neon

Introduction

When atoms are subjected to high temperatures or an electrical discharge, they emit electromagnetic radiation with characteristic frequencies. This phenomenon is used to identify elements in unknown samples or in distant stars by matching their spectra with those of known elements. The emission spectrum of atomic hydrogen consists of a series of sharp, well-defined lines. In this experiment, you will calibrate a spectrometer using the well-known lines in the hydrogen spectrum, then use the calibrated spectrometer to measure some of the transitions in the atomic spectra of mercury and krypton. You will use the atomic selection rules to identify likely transitions in those atoms.

Bohr's model of atomic structure of hydrogen invoked certain allowed circular orbits in which the electron could travel around the nucleus.[1] Thus, its energies are quantized and he spoke of the electron being in a particular energy level corresponding to a specific orbit. Using classical physics and Plank's quantum theory, based on the equation formulated by Rydberg, Bohr showed that the energies an electron can possess in the hydrogen atom are given by

$$E_n = -hcR_H \left(\frac{1}{n^2} \right) \tag{1},$$

where E_n is the energy of the electron in the nth level (n = 1, 2, 3…), h the Plank constant, and c the speed of light. The negative sign in this equation means that the allowed energies of the electron are less than the case in which the electron and the proton are infinitely separated, which is arbitrarily assigned to be zero. The more negative E_n is, the stronger the attraction between the electron and the proton. Thus, the most stable state is the one given by n = 1, which is the ground state. An excited state is one for which $n \geq 2$.

Eq. 1 provides a basis for analyzing the emission spectra of atomic hydrogen. Consider a certain electronic transition from a higher energy level (E_i) to a lower one (E_f), the condition for this transition is

$$\Delta E = E_f - E_i = hv \tag{2},$$

where hv is the energy of the emitted photon and $E_i > E_f$. In fact, all spectroscopy makes use of this relationship. The type of energy level might change (electronic, vibrational, rotational, nuclear, etc.), but the principle is the same: observed lines correspond to transitions between energy levels. Based on (1) and (2) we write

$$\Delta E = hv = hcR_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \tag{3}.$$

Hence, the wavenumbers observed were given by

$$\frac{v}{c} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \tag{4}.$$
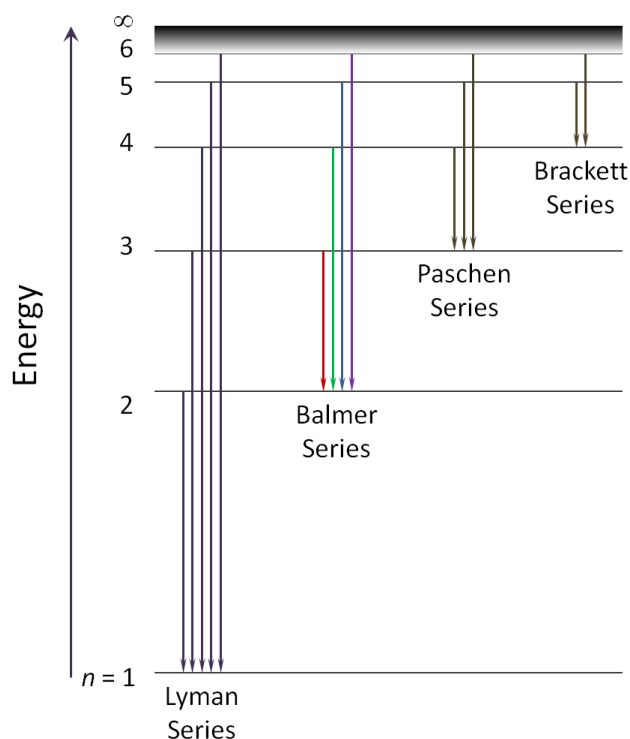
Figure 1. The atomic spectrum of the hydrogen atom. Note that only a small number of atomic transitions occur in the visible, and that none of them involve the ground state.

Figure 1 shows the energy-level diagram of the hydrogen atom and the various emissions that give rise to the different spectral series. Within a series, the value of the lower energy level (n_f) is the same. For example, for the Balmer series, which occurs largely in the visible range of the spectrum, $n_f = 2$.

Bohr's model is only useful for calculating single electron atomic spectra. Much more complicated calculations involving numerical estimates (i.e., not determined by evaluating an integral) are required for any element or ion with more than one electron. The atomic spectra were tabulated (and in many cases, collected or corrected) as the life's work of Charlotte Moore.[2] The Moore tables remain an invaluable resource for elemental analysis, as well as providing assignments to the transitions observed (beyond the Bohr approximation, which you will note does not include angular momentum). The different energy levels in many-electron atoms are identified by unique term symbols of the form L_J^{2S+1}, where L gives the orbital angular momentum of the highest occupied atomic orbital (S, P, D, F, etc. for L = 0, 1, 2, 3, etc.). Note that capital letters are used to denote the quantum numbers of atomic states, while lowercase letters are used to denote quantum numbers of individual electrons within an atom. S is the total spin, counting spin up as +½ and spin down as –½, and J is the total angular momentum quantum number, which can take any of the vector sums of L and S. Thus, for a given pair of L and S values, J can have values ranging from $|L - S|$ to $L + S$. The set of selection rules for atomic spectra are based on the angular momentum rules:

1. $\Delta l = \pm 1$: the electron which is excited or which emits must move up or down by exactly one unit of angular momentum, so that $s \to p$ is permitted, but neither $p \to p$ nor $p \to f$ are permitted.
2. $\Delta L = 0, \pm 1$: this rule applies to the term symbols for the different atomic states.
3. $\Delta J = 0, \pm 1$: L-S coupling mechanism can change, but in order to do so, it must receive a unit of angular momentum from the photon.
4. $\Delta S = 0$: No spin flips are permitted.

In reality, "forbidden" transitions are simply much weaker than "allowed" ones.

Spectrometry

A spectrometer may measure absorption (as in the PIAB experiments), or they may measure emission (as here). In either case, a spectrometer must disperse the wavelengths that enter so that the relative amounts of each wavelength can be measured. One way to accomplish this is with a prism: different wavelengths of light will be refracted to different extents, so that white light will be spread out at some distance from the prism

into the familiar visible spectrum. In this experiment, we will use a grating (Figure 2), a device which uses the interference properties of light to disperse it. A grating is a piece of material with many very closely spaced (spacing of lines is denoted d) lines etched into it.[3] Diffraction gratings work by destructively interfering the various wavelengths with one another except at a particular angle of scattering for each wavelength, where interference is constructive. The lines are etched somewhat at an angle, as shown in detail in the right of Figure 2. The grating equation relates the angle relative to the incident beam at which the light will be diffracted for a given order, m. Note that 0th order diffraction is not dispersed (but all others are):

$$d \sin \theta = m\lambda \hspace{3cm} (4).$$

Thus, we see that the sine of the dispersion angle is directly related to the wavelength of light being dispersed.
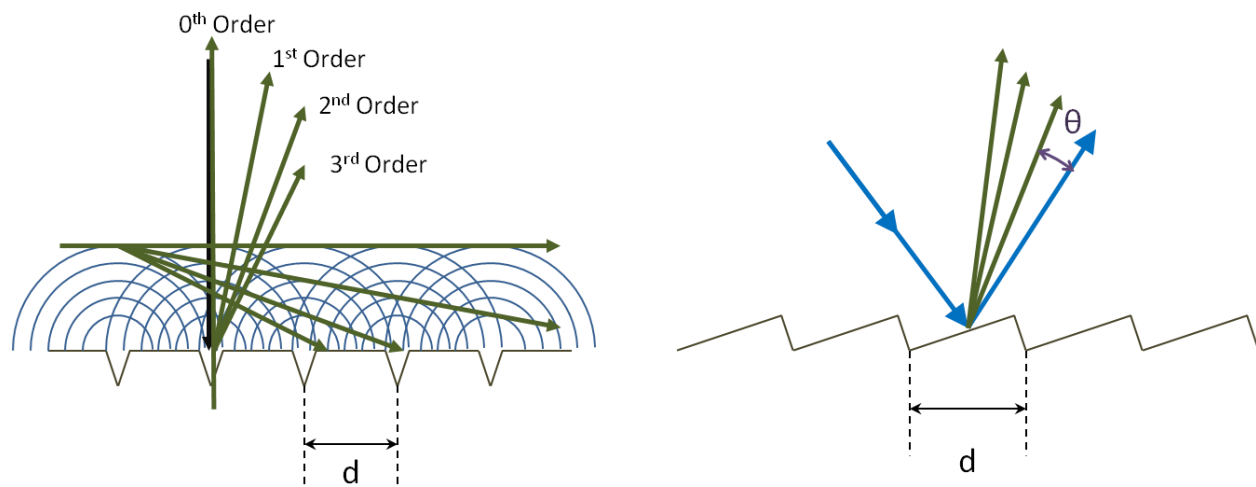
Figure 2. A diffraction grating (left) with line spacing d, showing several diffraction orders at different angles, θ. In each case, the order refers to the number of wavefronts offset between slits. 0th order diffraction is most intense, but does not disperse. In a typical spectrometer grating (right), incident radiation is not normal to the surface of the grating, and the slits are in fact a saw-tooth pattern.

Experimental Procedures

In this lab, you will use a digital monochromator with a charged-couple device (CCD) array detector. The first task is to calibrate using the hydrogen lamp. You should record the location of the lines (in pixel number) to calibrate the instrument– the software is capable of doing this, but you will do it using Excel. To calibrate, you will need to calculate the wavelength you expect for each of the transitions in the hydrogen atom. Follow the instructor directions to align the spectrometer, then collect data using the neon lamp. You will later correlate the lines with some possible transitions in neon, using data from Charlotte Moore's tables.

Data Analysis and Lab Reports: Informal Lab Report

This report is *informal*: you do not need to have all the usual sections. Instead, just answer the following in a brief, typed report. Figures and tables should still follow the same guidelines.

1. Create a table (with an explanatory caption) of the visible (300-800 nm) hydrogen lines in the Balmer Series which lists the initial and final values of n, the wavenumber (in cm⁻¹) of each, and the wavelength. Use this as your "calibration" between pixels and wavelength for the spectrometer. This is easiest

accomplished by creating a plot of wavelength as a function of pixel, and fitting a second order polynomial to data. The equation for this fit will give the wavelength for any peak detected by inserting the pixel value for the peak.

2. Discuss the average linewidth (do this in wavenumbers, not wavelength!) observed in your experiment. Is your linewidth limited by your instrument, or is it an inherent value? This linewidth is the uncertainty in your measurement.

3. Include a figure (with an explanatory caption) that shows a calibrated spectrum of the neon lamp. Identify at least three lines which are associated with neon. Use the tables provided to try to identify the transition (labeled by the appropriate pair of term symbols) to which the observed line could reasonably correspond. Pay attention to the selection rules in identifying these. Label the transitions *on your figure* that you have selected (not by hand: use an equation editor to do this).

4. Explain how atomic spectra could be used to determine the compositions of stars. Why is this less useful for colder systems like planets? Be careful about the distinction between absorption and emission spectra.

References

1. Engel, T., and Reid, P. *Physical Chemistry,* 4ed.; Pearson Education: Upper Saddle River, NJ, 2006; pp. 345-348.
2. Moore, C. E. *Selected Tables of Atomic Spectra, Volumes I-III.* Circular of the National Bureau of Standards 467, US Government Printing Office, Washington, D.C. (1958).
3. Fowles, G. R. *Introduction to Modern Optics,* 2ed.; Holt, Rinehart, and Winston: New York, 1975; pp. 122-125.