ATOMIC SPECTRA AND QUALITATIVE SPECTRAL ANALYSIS

1. The aim of the laboratory

The aim of these laboratory is: i) to observe the discrete spectra of two gases and to compare with the continuous spectrum of the natural light ii) to calibrate a spectroscope (to establish the relationship that exist between the position of the neon spectral lines observed on a scale and the wavelength) and iii) to use the calibration curve for the determination of mercury spectral lines wavelengths.

2. Theoretical approach

The Danish physicist Niels Bohr (1885-1962) studied the problem of the atom. He tried to unify the nuclear model with Einstein's quantum theory of light. In that time, 1911, Einstein's revolutionary theory of the photoelectric effect had not yet been confirmed and was not widely believed. Bohr accepted the planetary arrangement of electrons but made the hypothesis that the laws of electromagnetism do not operate inside atoms. He postulated that an electron into a stable orbit does not radiate energy. Therefore, the electron does not fall into the nucleus, destroying the atom. Bohr assumed that the light emitted by the hydrogen atoms accompanied changes in the energy of the electrons. He noted that the specific wavelengths in an atomic spectrum mean that an atomic electron cannot absorb or emit just any wavelength of light. According to Einstein, the energy of a light photon is given by $E = h\nu$. Thus, an electron can emit or absorb only specific amounts of energy. That is, the energy of an electron in an atom is quantized.

The different amounts of energy that an atomic electron is allowed are called energy levels. When an electron has the smallest allowed amount of energy, it occupies the lowest energy level. This level is called the ground state. If an electron absorbs energy it can undergo a transition to a higher level, called the excited state. Atomic electrons usually remain excited only a very small fraction of a second before returning to the ground state and thus emitting electromagnetic waves.

According to Bohr, the energy of an orbiting electron in an atom is the sum of the kinetic energy of the electron and the potential energy resulting from the Coulombian attraction force between the electron and nucleus. Work has to be done to move an electron from an orbit near the nucleus to one farther

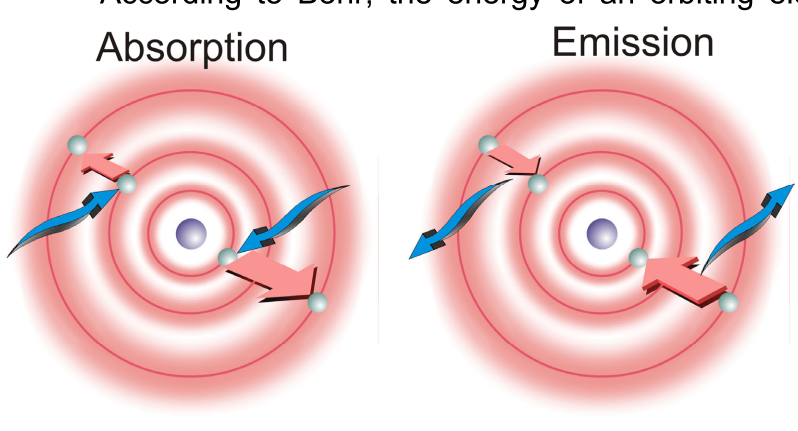

Figure 1

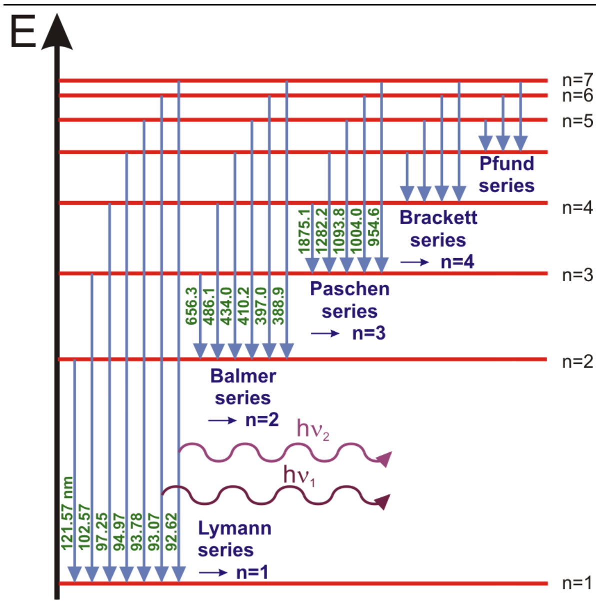

Figure. 2

away. Therefore, the energy of an electron from an orbit near the nucleus is less than that of an electron in an orbit farther away. The electrons into an excited states have larger orbits and thus higher energies. Einstein demonastrate that the light photon has an certan energy. Bohr postulated that an photon can be absorbed only if the energy of the photon is equal with the difference in the energy of the atomic electron levels (see also figs. 1 and 2). That is:

$$h\nu = E_{excited} - E_{ground}. \qquad (1)$$

When the electron makes the transition to the ground state, a photon is emitted (Fig. 1). The energy of the photon is equal to the energy difference between the excited and the ground states (see the Lymann series from Fig. 2). The molecules also have discrete energy levels. Furthermore, molecules have many ways to absorb energy. For example, they can rotate and vibrate along the bonds, which atoms cannot do. As a result, molecules can emit a much wider variety of light frequencies than atoms. While atomic spectra are discrete spectra of lines, the molecular spactra consist from many bands.

3. Fluorescence and Phosphorescence

There are three ways to cause the atoms to emit photons: thermal excitation, electronic excitation and photon excitation (see fig 3). Let us consider a fluorescent lamp filled with mercury vapour. When a high voltage is applied across the tube, the electrons collide with the Hg atoms, causing them to emit ultraviolet photons. These photons strike a material called a phosphor, coated on the inner surface of the glass tube. The ultraviolet photons are absorbed by the atoms in the phosphor.

The atoms and the molecules of the coated substance are excited, emitting photons of visible rather than ultraviolet light. Collision with photons, then, is another method of exciting atoms, besides the thermal excitation and the electron collision. Both fluorescent and phosphorescent materials contain atoms that are easily to be excited. The substances differ by the duration of time needed for excited atoms to relax to their normal energy levels. When an atom of a fluorescent material is in the excited state, the atoms return to their normal energy levels at once. In the higher energy levels the atoms have no stability. A phosphorescent material contains atoms that, once excited, can remain for some time in higher energy levels. Thus, a fluorescent reflector on an automobile will

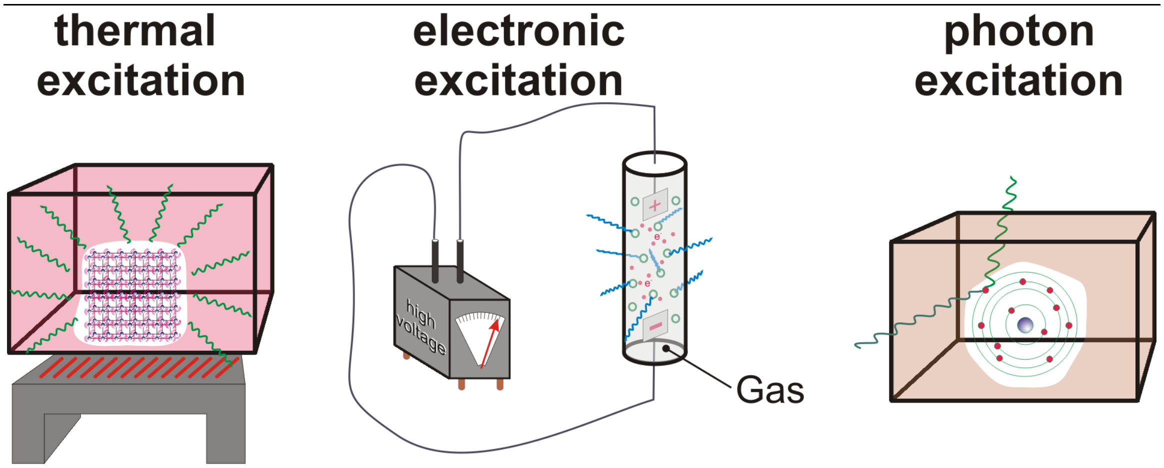

Figure 3

glow only while it is being irradiated by the photons from the headlights of another automobile. Thus, the coating of a fluorescent lamp emits light only when current flows through the tube.

Phosphorescence is somohow simmilar with fluorescence but can be observed also after the incident light is turned off. The atoms in phosphorescent materials remain longer in excited energy levels than in the case of fluorescent substances. There is no sharp border-line between fluorescence and phosphorescence. Generally, if an atom remains on an excited energy level longer than 10^{-3} seconds, then the substance is considered to be phosphorescent.

4. Atomic Spectra

The puzzle of the electron's positions and motion around the nucleus in atom was clarified by studying the light emitted by atoms. The set of wavelengths of light emitted by an atom is called the emission spectrum of that atom. When a body is heated it becomes incandescent. Moreover, all incandescent solids emits the same spectrum. The properties of individual atoms become apparent only when they are not tightly packed into a solid. Many substances can be vaporized by heating them into a flame. Then the atoms can emit light which is characteristic to each elements from the substance. For example, if sodium chloride is held in a flame, the sodium atoms will emit a bright yellow light. Similarly, lithium salts emit red light, and barium salts emit green light.

Gas atoms can be made to emit their characteristic colours by a electronic excitation (shown in fig. 3 middle). A glass tube containing neon gas (Ne) has metal electrodes at each end. When a high voltage is applied across the tube, electrons pass through the gas, the electrons collide with the neon atoms, transferring them the kinetic energy and exciting the Ne atoms. When they release the suppementary energy, this extra energy it is emitted in the form of light. The light has a red colour. Nitrogen and argon emit a bluish colour, and mercury, greenish blue. The emission spectrum of an atom can be studied in

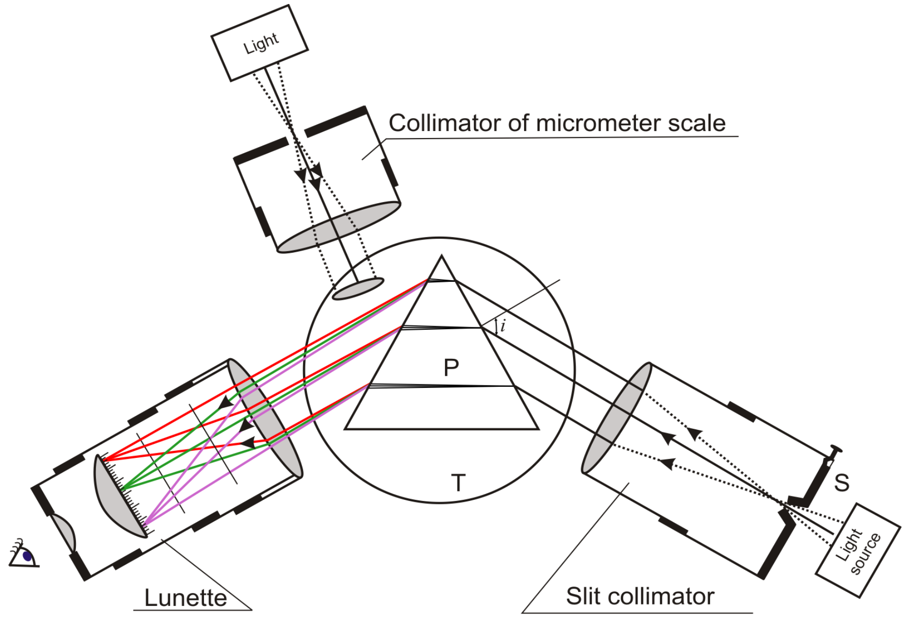

Figure 4

greater detail using the instrument shown in figure 4. In this spectroscope, the light passes through a slit (S) and is then dispersed by passing through a prism. A lens system focus the dispersed light which finaly is observed through a telescope. Each wavelength of light forms an image of the slit. The spectrum of an incandescent body is a continuous band of colours from red to violet. However, the spectrum of a gas is a series of lines of different colours. Each line corresponds to a particular wavelength of light emitted by the atoms. The emission spectra of atoms are characteristic features of the atoms of that gas.

5. Applications

Optical spectroscopy (which contain the visible, ultraviolet and infrared domains) allow the identification of constitutive elements from a material, determination of chemical structure, the establishment of concentration of a specific component from a material. The utility of spectroscopy as a measurement tool was demonstrated and now is applied in almost all domains of activity like: physics, astrophysics, chemistry, biology, medicine, food industry, etc. Some examples are the qualitative analysis of drugs, the identification and purity control of various substances, dosage of substances in mixtures.

6. Experimental Procedure

This experiment will focus on:

1. Observing the emission Ne spectrum, with the prism spectroscope. The wavelengths of the lines in the Ne spectrum are given in table 2 and the coordinates of the coloured lines are read on the spectroscope scale. All

being gathered in table 1. These data are then used to draw the calibration curve of the spectroscope, $\lambda=\lambda(\text{div})$.

2. Observing the emission spectrum of an unknown gas and finding out the wavelengths in its spectrum, by using the spectroscope for positioning the lines and the calibration graph to find their wavelengths. For a certain colour, of wavelength, its frequency is $\nu = c/\lambda$, and the energy of the photon emitted with this frequency is E = hν (J).

3. The second data table will be completed, considering all these and that the energy of photons is better to be expressed in eV ($1\text{eV} = 1.6 \cdot 10^{-19}\,\text{J}$).

Table 1

The studied substance	line color	bright red	red orange	orange	yellow	light green	left green	right green
Ne	wavelength (Å)							
	Line position (x)							

Table 2

The studied substance	line color					
Hg	wavelength (Å)					
	Line position (x)					

Table 3 Wavelengths of lines in the neon spectrum

Nr. Crt.	line color	relative magnitude	wavelength [Å]
1	bright red	10	6402
2	red orange	10	6143
3	orange	5	5945
4	yellow	20	5852
5	light green, first after yellow line	4	5760
6	left green	8	5400
7	right green	6	5330
8	green from right of those five equally spaced lines	5	5031
9	blue-green	8	4849